COLLOID SYMPOSIUM MONOGRAPH

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SYMPOSIUM ON COLLOID CHEMISTRY
UNIVERSITY OF MICHIGAN
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HARRY BOYER WEISER
PROFESSOR OF CHEMISTRY, THE RICE INSTITUTE

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FOREWORD

The Fifth Symposium on Colloid Chemistry, sponsored by the Colloid Division of the American Chemical Society, was held at the University of Michigan, Ann Arbor, Michigan, June 22, 23, and 24. Professor H. R. Kruyt of the University of Utrecht was the guest of honor. His paper on "Unity in the Theory of Colloids" furnished a fitting introduction to the series of papers published in full in this volume.

Before the close of the Meeting the 250 guests in attendance adopted unanimously the following resolutions:

"Resolved, that the members of the Colloid Symposium hereby express their appreciation of the delightful hospitality extended to us through President Little, Professor Bartell, and the various efficient local committees—a hospitality which has contributed so much to make this Symposium an outstanding event in the history of the development of colloid chemistry in America; and resolved, further, that we hereby express to Professor Kruyt our appreciation of his excellent paper and the illuminative contributions which he has made to the discussions which have made this meeting a real symposium in the true sense of the term."

The Sixth Annual Symposium will be held at the University of Toronto in June, 1928.

HARRY B. WEISER.

Houston, Texas.

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COLLOID SYMPOSIUM MONOGRAPH

UNITY IN THE THEORY OF COLLOIDS

By H. R. Kruyt

What is the aim of science? Not only to *know* but much more to *understand* nature; and we understand a phenomenon only when we recognize logic in it. So in science we try to discover logic in the behavior of matter. We meet every moment with phenomena which at first sight seem to be contradictory; then we try to reconcile them, *i.e.*, to raise the problem to a higher level, where the contradiction dissolves to a higher unity. We cannot be content as long as we have not found this unity, and therefore we are continually pursuing that goal.

Since we know that we are still far away from this end, however, we divide science into different branches: into biology, physics, chemistry, etc. For the present we are content if there is at least unity within the domain of each branch, and meanwhile we try (*e.g.* in physiology and in physical chemistry) to link these domains more or less together. Even these limitations, however, appear to be unsatisfactory; and consequently we come again to subdivisions and we limit our want for unification of theory to these smaller areas only. Here again we do not stop trying to join the different points of view; but we shall not be able to do so before we have understood each of the areas in a homogeneous way.

Now let us consider solutions. Ever since Selmi and Graham we have distinguished between "true" and "colloidal" solutions. Why? Because their behavior was contradictory. About 1890 physical chemistry accepted a theory of true solutions and paid no heed to colloidal solutions. Twenty years later, after a period of intense study on colloids, it was believed that the distinction between true and colloidal solutions was merely one of dispersity. It was overlooked that this was right only from a *morphological* point of view; the identity of all dispersed systems from the standpoint of the kinetic theory induced people to overemphasize this way of looking at the problem. *Energeti-*

cally, however, there was no continuity between the two classes of solutions and the problems of the relative stability of colloidal solutions remained as puzzling as before.

We shall show presently that this problem is treated in modern colloid chemistry in an absolutely *dualistic* way. Therefore one might think that perhaps the object of our special science is not homogeneous and that in colloid chemistry two fundamentally different systems are brought together. Thus we shall have to consider first of all what the object of colloid chemistry really is.

The historical viewpoint is not always the logical one, but Graham was a really scientific investigator. He may have been wrong in the contrast he made between colloids and crystalloids, but he was right in calling attention to the weak diffusibility of the colloids compared to that of matter in true solution. Nowadays we know the relations between the radius of particles and their diffusion, so we know that in colloidal solution we are dealing with relatively large, dispersed particles. I speak purposely of particles and not of molecules because from the standpoint of the kinetic theory there is no difference whether the particle is monomolecular or polymolecular. Take for example an arsenic trisulfide-sol; there is no doubt but that the molecule of arsenic trisulfide (As_2S_3) is built up of $2 + 3 = 5$ atoms, so it is a small molecule and the small diffusibility indicates that the particles in the sol are polymolecular. The same holds for a gold sol, a hydrous ferric oxide sol, etc.; also for a sol of sodium chloride in benzene and a sol of ice in a liquid which is immiscible with water. These polymolecular particles are characteristic of colloidal solutions and they can occur only when these particles do not tend to be split up by the dispersing medium to true (*i.e.* to molecularly dispersed) solutions.

Now, remarkably, everybody agrees when inorganic colloids are concerned, but when we come to certain organic colloids people suddenly take up the opposite point of view. Up to this point we have made a distinction between the size of the molecule given by chemical considerations and the size of the particle given by diffusibility and related properties such as osmotic pressure, depression of freezing point and vapor tension, all of which are hardly appreciable with colloids. With starch, agar, esterified cellulose, and the typical and classic colloids like glue and proteins, people say we have to do with very large molecules in true solutions. Why? The behavior of these systems is so much the same as that of the ordinary inorganic sols, that just for this reason they are brought together in the colloid group. There are, it is true, points of difference, but these are not related to the question of polymolecularity, as we shall see presently. We are misled by organic chemists who have said, for example, that the molecular formula of cellulose is $(C_6H_{10}O_5)_n$. This *n* was a product of fantasy. Cellulose cannot be brought into the gaseous form, nor can it be dissolved in

any liquid, so we cannot estimate its molecular weight. However, this is no different than the case of the arsenic trisulfide sol or the gold sol; but nobody ever says that their formulas are $(As_2S_3)_n$ or Au_n. Happily, in modern times X-ray analysis has thrown light on this question of the molecular size of insoluble matter, and a great number of organic chemists are conscious of the arbitrariness of this small *n* (Bergmann,[1] Hess, Karrer, Pringsheim, etc.). There is no doubt but that the particles in all these solutions are polymolecular.

The object of colloid chemistry (so far as liquid systems are concerned) is, therefore, the study of those systems in which polymolecular particles are dispersed. These systems are never so well defined as are true solutions, for the condition of true solution is a condition of *equilibrium*, a condition of minimum free energy, so the system always tends to get into that condition. The colloidal condition, on the other hand, does not represent a final equilibrium: If you put a lump of sugar into a beaker of distilled water, the result will be an absolutely definite solution; but if you do the same with a ten dollar gold piece, it will not become a red gold sol even if you wait an eternity, because the divided system gold-water has less free energy than the gold sol. We can get the sol only by a roundabout method; we must find a way to divide the matter into small particles and, in the meantime, create conditions which will give a certain (relative) stability to these particles in order to avoid their immediate coalescence. So the colloidal system is not stable, but it tends to get into another condition (aging phenomena). Every change in the method of preparation causes a change in the product which is formed.

If we want to understand the possibility of existence and the behavior of these colloidal systems, we must come to an understanding of the conditions of relative stability of these polymolecular particles and of the way in which matter is subdivided into these particles.

As to the stability of the so-called suspensoids or lyophobic colloids, everybody agrees that the Brownian movement would bring the particles together and surface tension then would cause their mutual adhesion if there were not an electric repulsion between the particles. Indeed cataphoresis proves the existence of the electric charge of the particles. Hardy,[2] Burton,[3] Powis[4] and other investigators have shown that a certain electrical charge of the particles is necessary to maintain a sol's stability for a certain time.

One of the most important problems of colloid chemistry is to know the character of this electrical charge. This has been shown by the way in which the charge disappears under the influence of electrolytes.

[1] See e.g. M. Bergmann, *Liebig's Ann.* **445**, 1 (1925); **448**, 76 (1926); *Z. angew. Chem.* **38**, 1141 (1925); *Naturw.* 13, 1045 (1925); P. Karrer, Einf. Chemie polymeres Kohlhydrates (Leipzig, 1925).
[2] *Z. physik. Chem.* 33, 385 (1900).
[3] *Phil. Mag.* (6) 11, 425; 12, 472 (1906); 17, 583 (1909).
[4] *Z. physik. Chem.* **89**, 186 (1915); *J. Chem. Soc.* **109**, 734 (1916).

The investigations of Schulze [5] and of Linder and Picton [6] on flocculation and those of Perrin,[7] Freundlich and Elissafoff [8] on electroendosmosis, of Kruyt [9] on potentials of flow and of Powis [4] on cataphoresis have shown that in all these cases we have to do with the same kind of electric charge. Characteristic in all these cases is the influence of the valency of the ion with an electric sign opposed to that of the particle, and the special influence of those ions, which Freundlich [10] and his pupils claimed to be very readily adsorbed. The order of these phenomena being the same in all the cases mentioned, they are to be explained by the same assumptions. Now Helmholtz [11] has given as early as 1879 his theory of the sliding double layer for all these electro-kinetic or capillary-electric phenomena; the need for unity in theory, therefore, brings the coagulation of suspensoids under the same viewpoint. We must admit immediately that the final word has not yet been said concerning the Helmholtz theory; moreover, the theory does not say anything about the influence of electrolytes, but Freundlich [10] has shown the connection between adsorption of electrolytes and their electric influence. Again it must be admitted that this theory is not gospel truth, but whoever denies these trains of thought must give another theory, which will explain the facts as well and which is not in conflict with other principles of electrochemistry and electrophysics.

So, although it may be granted that we still have much to learn about the character of the electrical charge of the suspensoids and about capillary electric phenomena, it is obvious that there is an enormous difference between the electrical behavior of a suspensoid particle and an ion of an electrolyte in a true solution. When dealing with true solutions of electrolytes we never find that an aluminum ion has 500 times the influence of a sodium ion,[6,10] nor has a fuchsine ion ever 10,000 times the effect of a potassium ion; [8] with these characteristic disproportionalities we deal only in the cases of colloid stability and of capillary electric phenomena.

As soon as lyophilic sols are concerned, however, most colloid chemists take quite a different point of view. Brailsford Robertson,[12] Wo. Pauli,[13] Jacques Loeb,[14] and Duclaux [15] (to mention only some of the most authoritative scientists) treat protein solutions as molecularly or

[5] *J. prakt. Chem.* (2) 25, 431 (1882); 27, 320 (1883).
[6] *J. Chem. Soc.*, 67, 63 (1895); 87, 1906 (1905).
[7] *J. chim. phys.* 2, 601 (1904); 3, 50 (1905).
[8] *Z. physik. Chem.* 79, 385 (1912).
[9] *Proc. Roy. Soc. Amsterdam*, 17, 615 (1914); 19, 1021 (1917); *Kolloid-Z.*, 22, 81 (1918); Doctor dissertation Utrecht 1927 of P. C. van der Willigen and of L. W. Jannsen (still unpublished).
[10] *Z. physik. Chem.* 73, 385 (1910); and H. Schucht, *ibid.* 85, 641 (1913); H. Morawitz, *Kolloidchem. Beihefte*, 1, 301 (1910).
[11] *Wied. Ann.* 7, 337 (1879).
[12] Physical Chemistry of the Proteins.
[13] Kolloidchemie der Eiweisskörper, Dresden & Leipzig, 1920.
[14] Proteins and the Theory of Colloidal Behavior, New York, 1922.
[15] Les Colloides, Paris, 1924.

ionically dispersed systems. Although I differ absolutely from them, I can understand very well how they came to this viewpoint.

First of all, there are relatively few investigations on the cataphoresis of lyophilic sols with addition of neutral salts; most attention is paid to the influence of the hydrogen and the hydroxyl ion. Accurate experiments of this kind are very difficult, the methods being hardly developed.

Then there are some marked differences from the behavior of the lyophobic sols. When electrically neutral, the emulsoids generally do not precipitate; their charge can easily be reversed, *e.g.* by changing pH (but also by the addition of other ions, though much less attention is paid to that fact).

In the third place, chief attention has been given to the proteins. Their character as amino acids induced investigators to look upon them as electrolytes; just because so much attention has been given to the influence of acids and bases, the reversal of the charge could easily be explained from the electrolyte point of view.

And finally, there is a psychological argument. Nearly all investigators in this domain are physiologists, and a physiologist is less free than a physical chemist. The latter chooses his problems at a certain moment in such a way that they suit in the stage of science at that moment; the physiologist has his problems suggested by his biological subjects. Of course, protein solutions are of eminent importance for physiology now as well as at a time when colloid chemistry was not sufficiently developed to solve the problems.

Investigations carried out in my laboratory during the last eight years (the greater part of which has until now been published only in Dutch)[16] have taught that it is no longer necessary to admit this dualism in colloid chemistry. On the contrary, we have stated the following facts: lyophilic sols are polymolecular dispersions; their electric charge is of exactly the same type as that of suspensoids; electric charge is as much a stability factor with lyophilic as with lyophobic sols, only we meet with the difference that in the latter case it is the only stability factor, while in the former, the well known hydration of the lyophilic particles plays a part of equal importance. Finally, we have stated that the importance of hydrogen-ion concentration has been very much exaggerated.

Let us begin with the character of the electric charge. As I said above, accurate measurements of the cataphoretic movement are very

[16] H. R. Kruyt & H. G. de Jong, *Z. physik. Chem.* **100**, 250 (1922); H. R. Kruyt, *Kolloid Z.* **31**, 338 (1922); (with W. A. N. Eggink) *Proc. Roy. Acad. Amsterdam* **26**, 43 (1923); (with H. J. C. Tendeloo) *ibid.* **27**, 377 (1924) and *J. Phys. Chem.* **29**, 1303 (1925); (with Miss J. E. M. van der Made) *Rec. trav. chim.* **42**, 277 (1923); (with J. Postma) *ibid.* **44**, 765 (1925); *Nature* **1923**, 827.

In Dutch: Doctor Dissertations at the University of Utrecht: H. G. de Jong (1921) H. Lier (1924) and H. J. C. Tendeloo (1926). Further: H. R. Kruyt, *Natuurwetensch. Tijdschr.* **1924**; *Chem. Weekb.* **22**, 473 (1925). Further: H. G. Bungenberg de Jong, *Rec. trav. chim.* **42**, 437 (1923); **43**, 35 and 189 (1924).

difficult especially with colorless lyophilic sols.[17] However, another method has given us valuable indications, viz., the measurement of the so-called "electroviscous effect." I might state in advance that we have confirmed a great many of our results, obtained in this simple way, by the much more troublesome method of cataphoretic measurements. Moreover, in a paper presented at the Fourth Colloid Symposium[18] I have called attention to the fact that the relation between cataphoresis and charge is not nearly so simple as colloid chemists thought up till now. Dr. van der Willigen has extended the experiments during the last year and confirmed our previous results.

We started purposely with lyophilic sols that were not protein sols; and in order to exclude in advance an explanation from the standpoint of the electrolyte theory we chose a carbohydrate, agar. A solution of one-seventh percent at 50° C. shows a viscosity 1.7 times that of water at the same temperature.

Now Dr. Bungenberg de Jong studied the influence of electrolytes, e.g. $BaCl_2$, on the viscosity of such a sol and he found that the first milli-equivalents added gave an important decrease of viscosity. Further addition had hardly any influence. This suggests immediately that we are dealing here with capillary electric phenomena, as in that case small amounts of electrolyte are always capable of removing the electric charge. A glance at Figure 1 will give further evidence: ordinates are the viscosities relative to that of water, abscissas, the concentrations of the added electrolytes. The curves for monovalent cations fall in the upper black band, those for bivalent in the second, etc. Now von Smoluchowski has proven that removal of the electric charge implies a decrease of viscosity, so we are allowed to look upon this decrease of viscosity as a decrease in electrical charge and to conclude that the influence of electrolytes on the charge of emulsoids is not different from that on suspensoids. Further investigations of de Jong on starch sol gave as striking results; even the reversal of the charge (as with the so called "irregular series" in colloid flocculation) could be observed with a hexavalent complex cobalt ion. With inorganic sols of cerium oxide and silica we found similar results; even rubber in benzene showed analogous phenomena.

We came to the conclusion that most lyophilic sols do not precipitate, although their electric charge has been removed, because another stabilizing factor prevents flocculation. Evidently this factor is the hydration, for the removal of this hydration by the addition of any dehydrating agent causes flocculation by electrolytes.

If sufficient alcohol or acetone is added to the sol of agar, starch, gelatine or any other emulsoid sol, the sol turns into a lyophobic one: its viscosity deceases practically to a value corresponding with that of the

[17] Cf. H. R. Kruyt, *Kolloid-Z.* **37**, 358 (1925).
[18] "Colloid Symposium Monograph," Vol. 4, 304. Chemical Catalog Co., New York, 1926.

disperse medium. As, according to Einstein's formula, the relative viscosity of a disperse system is merely a function of the total volume of its particles, the latter must be very much decreased; this can only be explained by a dehydration of the particles. Following this decrease in viscosity all sorts of suspensoid properties have come to the sol: salts flocculate it in just the same way as they do arsenic trisulfide sol or a gold sol; the sol often gets the opalescent appearance of a mastic sol with particles visible in the ultramicroscope.

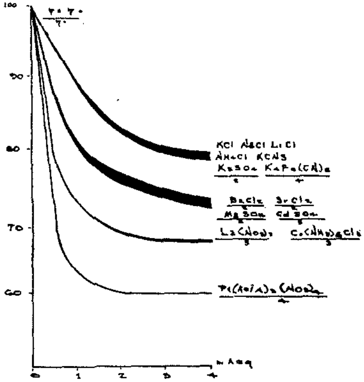


FIG. 1.

The salting-out phenomena now can be easily understood. When magnesium chloride is added to an agar sol, the first millimols added take away the charge of the particles; we find by measuring the electroviscous effect (see Fig. 2) that further addition has hardly any influence on the relative viscosity. If we add magnesium sulfate we first deal with quite the same phenomenon, but here, further addition causes a further decrease of relative viscosity, by the dehydration of the particles, and we soon have a precipitation (salting-out effect), as dehydration of discharged particles must necessarily cause flocculation.

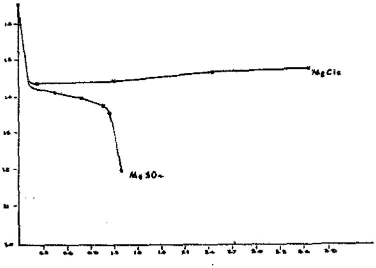


FIG. 2.

This dehydration by electrolytes can be connected by their lyotropic position, sulfate ion being normally much more active than chloride ion

under the conditions of this experiment. Consequently, magnesium chloride does not effect a continuous decrease in relative viscosity nor a *precipitation (salting out)* of agar; magnesium sulfate, however, causes both.

Does this way of looking at lyophilic sols hold for protein sols? To answer this question we put it first of all in this way: has the electric charge of a protein particle really the character of capillary electricity? Lier and the writer studied casein sols from this standpoint and found a behavior corresponding in every respect to that of agar, as given in Figure 1, when we added mono-, di- and trivalent cations to the negative sol (casein dissolved in alkaline solution) or mono-, di- and trivalent anions to the positive sol (casein in acid solution). In Figure 3 we give schematically our results with the negative casein sol. Ordinates are the relative viscosities and abscissas the concentrations of added electrolytes. The main curve gives the viscosity independent of hydroxyl-ion concentration. If we take a sol with the viscosity a, for instance, and add sodium chloride, barium chloride or luteocobalt chloride we find viscosities as given by the thin curves. Thus we proved that indeed we deal here again with capillary electric phenomena and consequently there must be a phase boundary, where this capillary electric charge is located; necessarily, we are dealing with polymolecular particles and not with dispersed molecules nor ions.

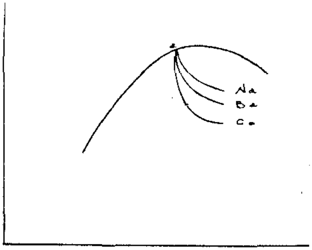


FIG. 3.

The special influence of the hydrogen ion and the hydroxyl ion are readily understood when we keep in mind that acids and bases will interact with the molecules at the periphery of the particle. These amino acid molecules will give substituted ammonium salts of the type $R\text{-}NH_3.Cl$ with hydrochloric acid and salts of the type $R\text{-}COO.Na$ with NaOH. These very polar groups tend to place themselves perpendicular to the water boundary according to the theories of I. Langmuir and W. D. Harkins and thus give rise to an electric double layer.

In Figures 4 and 5 we give a schematic picture of such particles.

The special influence of the hydrogen and the hydroxyl ions on protein sols is thus a consequence of their ability to build up an electric double layer, of inducing a charge or taking it away: the hydrogen ion effecting an increase of positive or a decrease of negative charge,

the hydroxyl ion behaving in just the opposite way. The existence of an isoelectric point as a point of minimum viscosity will be readily understood: the electric charge must be zero at a definite pH, where the sol changes its sign; the electro-viscous effect must be zero at the same pH value. This alone would account for the minimum viscosity at the isoelectric point, but we are conscious that other investigators are also right, that there is some relation between charge and hydration. Although it is very difficult to get an insight into the quantitative

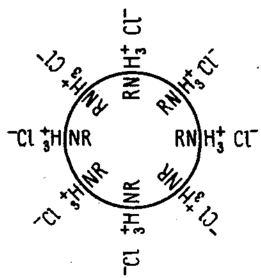


FIG. 4.

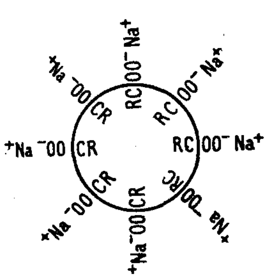


FIG. 5.

relation between these two values, it is very probable that a minimum hydration coincides with the charge zero, i.e. at the isoelectric point.

Granting, however, that increasing or diminishing a charge is by no means a special prerogative of the hydrogen and the hydroxyl ions, though for special chemical reasons they are with proteins in a somewhat privileged condition, all of our experience with suspensoids and with electrokinetic processes has taught us that polyvalent ions are also very active in these respects. Tendeloo and the writer [19] proved that the reversal of charge with gelatin, with all its accompanying phenomena, is not restricted to changes in hydrogen-ion concentration but can be brought about as well by other ions, in complete harmony with all that was to be expected from the standpoint of capillary electric phenomena.

Some proteins are so highly hydrated that their hydration alone is sufficient to stabilize their sols: they do not flocculate when deprived of their electric charge (gelatin, albumin). Others are not sufficiently hydrated (casein, globulin) in pure water; they are not sufficiently charged and they give no stable sols, but when an appropriate peptizing electrolyte is added, the charge, in addition to the small hydration, will

[19] *Loc. cit.*

give a sol. Therefore these protein sols are not stable in the neighborhood of their isoelectric point.

So we come to the conclusion that all colloidal sols, both lyophobic and lyophilic, have an electric character which we know as being of the type of boundary-electricity, of electroösmosis, cataphoresis and flow potentials. Electrolytes in true solution do not show such behavior since these phenomena set in only when phase boundaries are present. Polymolecular particles therefore are the constituents of all sols. We can treat them from a homogeneous standpoint and we can rejoice at the reconquered unity.

Innumerable facts confirm this train of thought; this is not the place to enumerate them. We might only call attention to one group already mentioned above, viz. the modern Röntgenographic investigations on cellulose, starch, etc. The investigations have shown that in many cases the primary cells are so small that the real molecules of these carbohydrates contain probably 6 or 12 carbon atoms (24 is the rather improbable maximum). On the other hand, the kinetically active particles are so much larger that they must be built up by several hundreds of those molecules. Moreover, Bergmann and Pringsheim [20] really isolated molecular $C_6H_{10}O_5$ as well as higher aggregates, all being equally cellulose. With the proteins we have not progressed so far but several facts point in the same direction, and experience in the physico-chemical field of colloidal chemistry together with X-ray investigations will come to a similar conclusion.

The authors who take up the other point of view and look on lyophilic sols as if these were true ionic solutions, have emphasized mainly two arguments. In the first place they think that reactions of proteins are stoichiometric. Loeb,[21] for instance, thought that a gelatin sol was brought from one pH to another by stoichiometric amounts of mono-, di- or tribasic acids. Hoffmann and Gortner [22] have pointed out clearly that this is not true. However, even if it were true it would not prove what is pretended, for in a given sol there is a given number of molecules at the periphery of the particles to act with the (acid) molecules in the external liquid. Nobody ever proved that *all* the gelatin molecules present reacted with the added acids, but only that an *equal* number reacted in two samples taken from the same solution; and because it was an equal number it was postulated that it was all the molecules.

A second argument is as insufficient as the first: it is the fact that Donnan's rule [23] for the equality of ion products at both sides of a membrane holds for lyophilic sols. Here we deal with an absolute misunderstanding of the theory put forth by Donnan. Accidentally

[20] *Loc. cit.*
[21] *Loc. cit.*
[22] "Colloid Symposium Monograph," Vol. 2, 209 (1924).
[23] *J. Chem. Soc.* **99**, 1554 (1910).

Donnan gave as the classic example for his theory, the case of Congo red, which is really an ionic disperse system with one ion that does not pass collodion nor parchment. Donnan used this example but the peculiar condition of this system does not come into his calculation at all. He derived the equation from general thermodynamic principles and his conclusion holds always, when ions are bound to certain particles that can pass and to others that cannot pass the membrane. It is absolutely arbitrary whether these particles are colloidal particles or large ions. Harmony between experiments and calculations according to Donnan's equation therefore cannot decide whether we deal with ions or with colloidal particles. Donnan himself is of the same opinion as expressed here.[24]

Moreover, Loeb's theory has failed completely to explain the electric behavior of protein sols. His last investigations[25] before his deplorable death showed that the electric charges play a rôle in colloid chemistry that are not at all identical with those calculated from Donnan's theory of membrane potentials. Not that Donnan's theory is wrong, but it refers to quite other potentials than we deal with in *e.g.* cataphoretic experiments (difference between transversal and tangential potential gradients). Again, only the conception of the colloidal particle as a polymolecular phase can lead us to a theory of the double layer that includes the different electric potentials active at the phase boundary.

There is still one point left to be discussed here. We have already said that our point of view must enable us to understand not only the stability conditions, but also the way in which matter gets into colloidal division. We shall not discuss so-called condensation methods, but only dispersion, i.e., those cases in which we start from the solid mass and bring it into colloidal solution.

Here we meet with a puzzling problem: we have said already that we do not get a gold sol when we shake a piece of gold with water, nor if we boil it; but when we heat starch or gelatin with water, we do get a sol. However this has nothing to do with the difference between lyophilic and lyophobic sols, for boiling a stone pebble does not give the (lyophilic) silicic acid sols. We can understand the problem if we pay attention to a transition case such as stannic acid. We see once more that a crystal of tinstone cannot be brought into colloidal solution, but the various forms of stannic acid (alpha-, beta- and meta-stannic acid) give sols, each very different, depending on the method of preparing the stannic acid and the subsequent treatment. Mecklenburg[26] pointed out that the main question was, how the particles were in the solid mass that is to be peptized; he and Zsigmondy[27] developed this

[24] *Chem. Reviews* 1, 73 (1924); cf. also Rinde, *Phil. Mag.* 1, 32 (1926).
[25] *J. Gen. Physiol.* 5 and 6 (1923-24).
[26] *Z. anorg. Chem.* 4, 207 (1912).
[27] "Kolloidchemie," 5th Edition, 39 *et seq.* and 179 *et seq.*, Leipzig.

trend of thought and called attention to the fact that the colloidal particles are formed in the solid material. When this is one large crystal, no peptization is possible. When the primary particles are all free "protons," then we get a highly disperse sol; when they stick together as "polyons," these will be the unities in the sol, which will therefore be coarse.

So a necessary condition for dispersing is the preformation of particles of colloidal dimensions, not reciprocally bound by fields of force, which are more or less homogeneously distributed (like the cells in a crystal), but bound at distinct points so loosely that they can be easily split up. By what forces? By the effect of a wedge, driven in either by an electric repulsion, consequent upon an electric charge brought about the surface of the two particles or by water molecules attracted by these. Suspensoid peptization has always the former character (SnO_2 with KOH, HgS with H_2S, etc.), emulsoid sol-building, mostly the second. However, we must make the assumption that these primary particles are already formed, say in gelatin, agar, albumen, etc.

Obviously such is the case. All these emulsoids (Freundlich[28] has called them xero colloids) are formed in organic nature, where cell after cell is formed as a unit. When we make an agar sol from an agar thread, we do not peptize one unit, as when we try to peptize a stone pebble in water, but we have the agar particles already formed in the seaweed; the latter has been treated in such a way that no definite coalescence of primary particles has taken place. However, when we precipitate agar with alcohol and an electrolyte, the coagulation is not reversible, as the particles, deprived of all their stability factors, stick together in such a way that they cannot be peptized any more by simple dilution. Apparently the same is the case with heat-coagulation of proteins; we are still investigating this topic. On the other hand, all that we said of agar holds as well for proteins, for rubber, etc.

When we look back to what we have stated above, we come to the conclusion that the colloidal solutions, both of lyophobic and of lyophilic sols, are built up of *polymolecular particles,* and that in both groups the *electrical character is the same,* viz., it has the electro-capillary (electro-kinetic) character. In this respect they therefore are *quite different from ionic disperse systems* and a theory which seeks for scientific unity by identifying lyophilic colloids to ionic solutions is on the wrong track. All colloidal solutions are principally of the same type and the first aim of colloid chemistry should be the better understanding of the electrical double layer, as this comes to the fore at all sorts of boundaries.

Utrecht, van't Hoff Laboratory.
March, 1927.

[28] "Kapillarchemie," 2nd Edition, 908 (1922), Leipzig.

THE STABILITY OF EMULSIONS, MONOMOLECULAR AND POLYMOLECULAR FILMS, THICKNESS OF THE WATER FILM ON SALT SOLUTIONS, AND THE SPREADING OF LIQUIDS.

By William D. Harkins

I. Films

During the last few years, investigations which relate to certain fundamental properties of colloidal systems have been carried out at the University of Chicago, and the present paper will outline some of the results obtained, particularly in such cases as have given definite numerical magnitudes. One of the questions raised most often in the last decade concerns the extent to which films are monomolecular and to what extent they are polymolecular.

Monomolecular and Polymolecular Films.—That certain liquids spread out into a film one molecule thick on water was indicated in 1899 by Lord Rayleigh,[1] and more definitely by Devaux,[2] who began his researches on this subject in 1903. The idea that the polar groups, such as — COOH, of organic molecules are responsible for their spreading on water to films one molecule thick [*] was advanced in lectures presented early in the year 1914, as is shown by the photographic reproduction presented in Figure 1. This gives the fundamental idea of the orientation theory as presented in connection with a discussion of the forces involved in the spreading of oleic acid on water, in the terse expression: "COOH of acid down because both acid and water associated and polar." Thus the spreading of oleic acid on water was supposed to be due to the high specific attraction of the polar carboxyl (— COOH) group for the polar water, which results both in an orientation of the molecules of the oleic acid on the surface, and the spreading into a monomolecular film. So much attention has been given more recently to the formation of such monomolecular films, that the present section will be devoted almost entirely to the question of thicker or polymolecular films.

[1] *Phil. Mag.*, 28, 331 (1899).

[2] Papers 103-13 reviewed in *Ann. Report Smithsonian Inst.*, 1913, pp. 261-73; *Soc. Franc. Phys.*, 55, 3 (1914); 57, 3 (1914).

[*] That molecules are oriented in surfaces was suggested in 1912 by Hardy. His suggestions are given verbatim in a paper by the writer in "Colloid Symposium Monograph," Vol. 2.

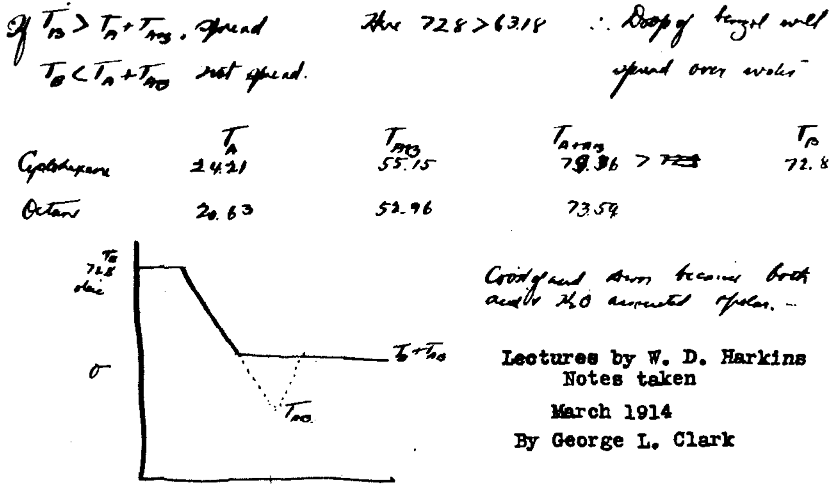

Cyclohexane 24.21 55.15 72.8
Octane 20.63 52.96 73.54
Lectures by W. D. Harkins
Notes taken
March 1914
By George L. Clark

Fig. 1.

The lower part of Figure 1 gives at the left a plot which exhibits the lowering of the tension of water (γ axis) as produced by a film of oleic acid. Decrease of the x-coordinate represents a decrease in area of the film. Now the compressive force on the film (F) may be defined by the relation

$$\gamma_{\text{pure water}} - \gamma_{\text{water plus film}} = F$$

In Figure 2, F is represented on the y-axis, and the area per molecule on the x-axis. It is evident that Figure 2 is merely Figure 1 inverted.

That this conception of the variation of the compressive force was entirely justified is shown by Figure 3, which represents experiments on monomolecular films of stearic acid on water.

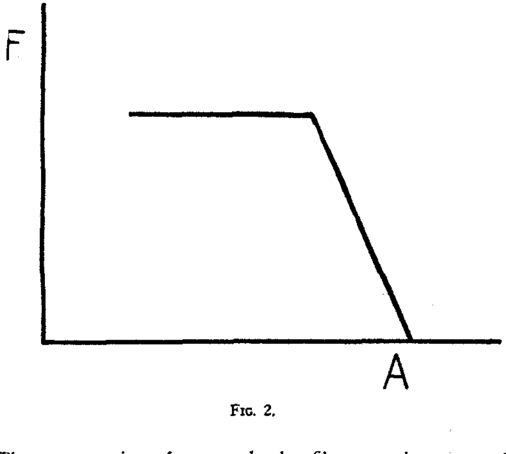


FIG. 2.

The concentration of monomolecular films may be expressed in terms of the area of surface covered per molecule of film, since the surface concentration varies inversely as this area. In the case of polymolecular films it is useful to consider a mean thickness of the film. The apparent mean thickness (τ) is defined as the thickness which the film would have if it were spread with perfect uniformity over the surface and were to have the same density as that exhibited by the pure material in bulk.

The greatest mean thickness of the monomolecular film of palmitic acid is 30A° (1A° = 10^{-8} cm.), while its smallest area per molecule is 18.4 A² (1A² = 10^{-16} sq. cm.). These values give some criterion as to what may be expected if polymolecular films are produced. Thus if uni-

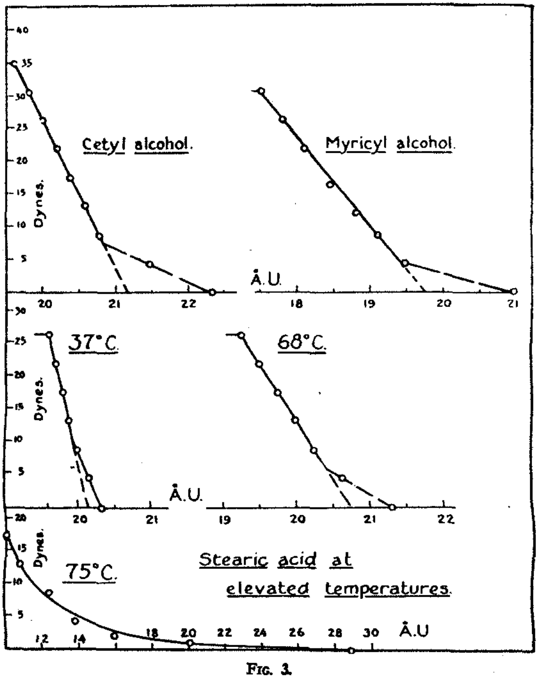


FIG. 3.

form films of stearic acid of several times this mean thickness, or with a very much smaller area per molecule, are formed, it might be assumed that polymolecular films have been produced. However, attempts to form such polymolecular films of palmitic acid have in no case been successful. Neither has it been found possible to form such films in any

case in which all of the molecules of the substance used contain polar groups; such as — COOH, — OH, NH_2 — CO or H_2, — SH, etc.

Spreading in the Absence of Polar Groups. While the presence of polar groups in the organic substance is thus seen to give rise to spreading to form monomolecular films on water, the behavior in the absence of polar groups is not indicated. Earlier work in this laboratory [3] showed conclusively that the presence of polar groups in organic substances is not essential for spreading to occur, since not only benzene, but also hexane, heptane, and octane spread readily provided the surface of the water is pure.

Indeed, as has already been shown the criterion for spreading or non-spreading is not based upon the presence or absence of polar groups, but may be stated: If F is positive the liquid will spread, but if F is negative it will not spread. Now F is ordinarily used to represent a force, but the criterion of spreading may be developed from thermodynamics if instead the decrease in free energy (S) which accompanies the spreading, is considered.

$$S = \gamma_A - \gamma_F$$

Here γ_A is the force energy per unit area of the surface on which the spreading is to occur, and γ_F is the free surface with the film present. Numerically S is equal to F.

However, if instead of a film, a thin layer of the upper liquid is present,

$$S = \gamma_A - (\gamma_B + \gamma_{AB})$$

in which γ_B is the free surface energy of the upper layer and γ_{AB} is the interfacial free energy. From this equation it is easy to show that

$$S = W_a - W_c$$

or spreading occurs if the interfacial work of adhesion between the liquids is greater than the surface work of cohesion in the liquid.

II. The Measurement of Polymolecular Films

(Experiments with J. W. Morgan)

By the use of a film balance it is possible to measure directly the force (F) necessary to compress an insoluble non-volatile film. The difficulty involved in the measurement of this quantity with polymolecular

[3] Harkins and Feldman, *J. Am. Chem. Soc.*, **43**, 2665 (1921).

films is due to several factors. First, the substance must be non-polar, or only slightly polar. Otherwise it will spread into a monomolecular and not a polymolecular film. Second, most organic substances with small molecules are volatile, while if the molecules are large enough to be non-volatile and insoluble, their internal cohesion and thus the value of W_c, is so high that $W_a - W_c$ is negative; that is, they will not spread.

It is extremely difficult to find substances which will meet all of the conditions, so it is not surprising that up to the present time only two substances have been found which will give polymolecular films on water.

These are di-β-naphthylamine and symmetrical di-β-triphenyl ethyl urea, and these were found only by the application of ideas as to what classes of substances might meet the conditions for spreading.

It is evident that if the value of the work of adhesion could he increased, certain substances which otherwise would not spread would be caused to spread.

The increase of the work of adhesion was brought about by the addition of calcium chloride. With a 40 per cent aqueous solution of this salt polymolecular films were obtained with phenanthrene and other substances listed in Table 1.

TABLE 1.—FILMS ARRANGED IN ORDER OF INCREASING THICKNESS AT COLLAPSE. Dimensions in Angstrom units. $CaCl_2$ represents an aqueous solution of the salt.

Substance of Film	On	At Zero Force Area	At Zero Force Thickness	At Collapse Area	At Collapse Thickness
Monomolecular Films					
Phenyl dibiphenyl methyl amine	$CaCl_2$	112	6	80	8.4
Phenanthrol	Ca_2Cl_2	36.5	7	21.3	12
Stearic acid	H_2O	19.3	28.5	18.4	30
Symmetrical di-β-triphenyl ethyl urea	$CaCl_2$	77.5	12.2	68	14
Polymolecular Films					
Symmetrical di-β-triphenyl ethyl urea	H_2O	28.3	33.4	22.6	42
9,10-Dibromo anthracene	$CaCl_2$	5.9	47	2.5	111
Triphenyl methyl cyanide	$CaCl_2$	5.2	70	5	120
Phenanthrene	$CaCl_2$	5.6	47	2	132
Di-β-naphthylamine	H_2O	2.7	125.6	2.15	158
Hexachlorobenzene	$CaCl_2$	5.2	45	0.95	248
α-Bromonaphthalene	$CaCl_2$	1.5	187	0.6	405

While monomolecular films rarely reach an apparent mean thickness greater than 40 A° before they collapse, the polymolecular films produced by pure substances attain thicknesses of from 110 to 400 A°. These are the values at the highest attainable pressure on the film. At pressures so low that they were not measurable on the balance used,

the lowest mean thickness varied from 45 A° for hexachlorobenzene to 187 A° for α-bromonaphthalene. Thus under the action of a relatively low pressure these films are polymolecular.

The polymolecular films produced by pure substances show the following characteristics:

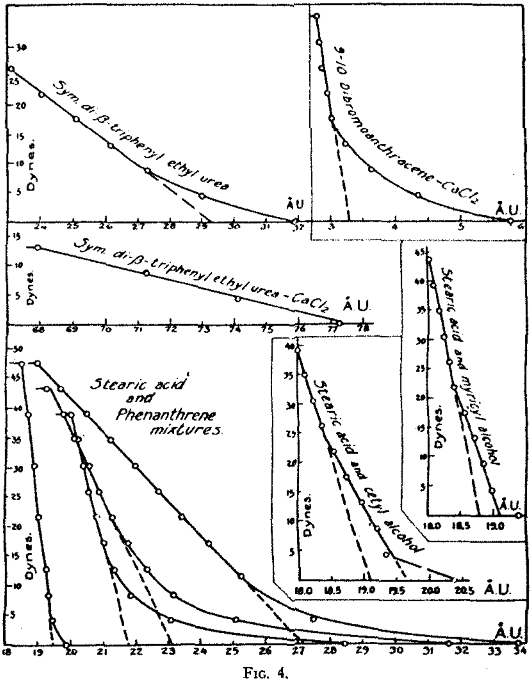


FIG. 4.

1. They are weaker than the monomolecular films usually measured.
2. Under compression at high pressures they usually exhibit a linear relation between compressive force and molecular area, which is what is found for monomolecular films.

3. They are very thin. Even the thickest polymolecular film thus far obtained has a thickness of only about one-tenth the shortest wave-length of visible light.

The film of dibromoanthracene is visible in a strong light almost parallel with the surface, which suggests that it is crystalline and that many points rise far above the general level. This is also true of di-β-naphthylamine on water and of anthracene on the calcium chloride solution. In some cases the film seems to consist of transparent flakes, which may be photographed.

Strength of Films.—Young's modulus for steel is about 12,000. For a monomolecular film, stearic acid on water, it is 39 and on a calcium chloride solution less than this. A polymolecular film is in general much weaker than a monomolecular film. Thus the value for dibromoanthracene is less than 2.

Films of Mixed Substances.—If two substances, each of which forms a monomolecular film, are mixed, the mixture forms a monomolecular film. The behavior of two such "mixed" films of stearic acid with either cetyl alcohol or myricyl alcohol is illustrated at the bottom of Figure 4.

Mixtures of stearic acid and phenanthrene give polymolecular films. Thus with 1 molecule of phenanthrene to 2.58 of stearic acid the area per molecule of the latter is practically the same as when it is alone. With 3.7 parts of the former to 1 of the latter the zero area per molecule of acid is increased only very slightly from 19.3 to 21.7. The curves at the bottom of Figure 4 (left side) are arranged in order of increasing percentage of phenanthrene and the arc plotted is that per molecule of stearic acid. With 6.4 molecules of phenanthrene the extrapolated zero area is increased only to 23, and with 16.4 to 1 to 27. It is thus evident that when the relation between force of compression and area is linear, as it is over a considerable range, almost all of the phenanthrene is piled up over the stearic acid, which forms a monomolecular layer underneath it.

Strength of Mixed Films.—The film which consists of 1 molecule of phenanthrene to 2.58 of stearic acid is as strong as or stronger than a film of the acid alone, but the strength decreases if much more phenanthrene is present, as shown in Table 2.

TABLE 2.—STRENGTH OF MIXED FILMS

Phenanthrene	Stearic Acid	Young's Modulus
0	Pure	35.83
1	2.58	37.5
3.7	1	6.7
6.4	1	2.64
16.4	1	0.9 cloudy film
Pure	0	1.45 at collapse 0.04 at zero

All of these mixtures exhibit a curved lower portion, but with 16.4 molecules of phenanthrene to one of stearic acid there is no apparent force required to compress the film until the area per molecule of the latter has been decreased to 34 A.U., or the area per molecule in the film has decreased to 1.95 A.U. Thus this film has attained a mean thickness of about 135A° before the force need to compress it becomes apparent. At collapse this film is about 240A° thick, which is much thicker than with phenanthrene alone. It is evident that the collapse of such a film occurs only when the stearic acid is torn away from the water, since the area per molecule of stearic acid at collapse in these mixed films is almost the same as with the acid alone. The addition of phenanthrene, which contains no polar group, changes considerably the actual zero area, has only a small effect upon the extrapolated (from the straight line) zero area, and almost no effect upon the area of collapse.

The results here reported for polymolecular films should be considered only preliminary in nature. The work is now being repeated by Professor B. B. Freud of Armour Institute of Technology. He expects to determine the effects at low film pressures, and also to avoid as much as is possible any contamination due to impurities in the calcium chloride or other salts used.

III. A Method for the Determination of the Stability of Emulsions

(Experiments with Norvil Beeman)

Several years ago the writer was very much surprised to find that no method for determining the degree of stability of an emulsion seemed to have been published, so experiments were begun in the laboratory for this purpose. The method developed consisted in determining the distribution of size of the droplets in a freshly prepared emulsion and at intervals later. The stability may be expressed by the distribution curves themselves, or the change of area per unit volume of oil may be considered.

A stable emulsion (Fig. 5) exhibits no change in this area, nor in the distribution of sizes. If a concentrated emulsion is used, the portion subjected to test is diluted by water or by a solution such that the distribution of size is not changed during the test. The distribution of sizes is then determined by the rate of rise of the droplets as determined by a photographic optical method,[4] by a density method,[5] or

[4] Stamm, "Colloid Symposium Monograph" 3, 251 (1925).
[5] Kraemer and Stamm, *J. Am. Chem. Soc.*, 46, 2709 (1924).

by direct microscopic measurement [6] of the droplets themselves. Figure 6 shows the variation of a distribution curve between the first day (fresh emulsion), and the third and seventh days. These particular tests were made on concentrated octane emulsions (87% oil) produced by either 0.005 molar sodium oleate or caesium oleate. It is evident that the interfacial area decreases rapidly with the time, so the fresh emulsions are quite unstable.

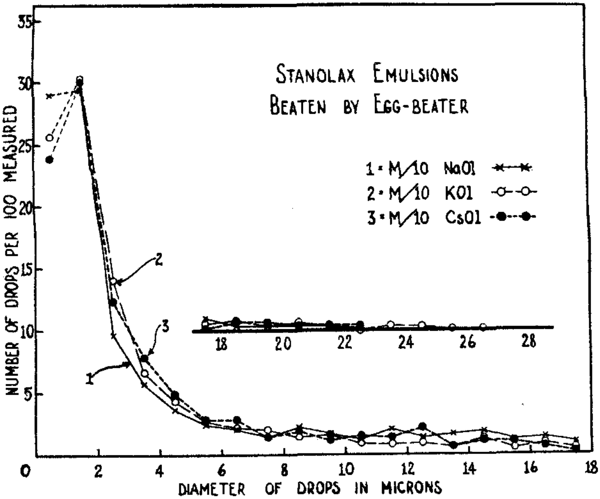


FIG. 5.

The Stability of Emulsions as Related to the Concentration of Soap in the Monomolecular Film.—Immediately after preparation the emulsion produced by 0.005M sodium oleate (Fig. 7) exhibited an area of 25,500 sq. cm. per cu. cm. of oil, but after three days standing this was reduced to 14,600 sq. cm. With caesium oleate the corresponding values were practically the same (25,000 and 13,800). It is evident that the concentration of soap in the monomolecular film increases rapidly with the time.

[6] Finkle, Draper and Hildebrand, *J. Am. Chem. Soc.*, 45, 3156 (1923).

That the film of soap corresponds to a moderately dilute monomolecular film is indicated by the fact that the area per molecule of soap in the film was found to be 61 A^2 and 64 A^2 for emulsions produced by

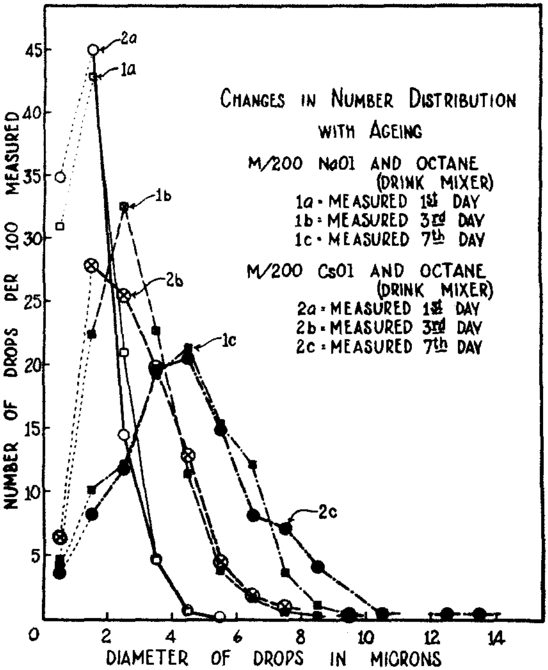


FIG. 6.

0.005 and 0.01 molar soaps, respectively. These values were obtained two days after the emulsion was prepared. The area per molecule in these interfaces is almost exactly three times that of oleic acid in a condensed monomolecular film on water.

While the area per molecule of soap was found to decrease with the time for more than nine days when the emulsifying agent was such a dilute soap, with 0.1 molar soap little or no decrease was observed. Thus practically no change was observed in the distribution of sizes in certain emulsions produced with 0.1 molar soap in the course of a year of standing at rest.

All of the emulsions under consideration were produced by the use of equal volumes of oil and water, and were therefore highly con-

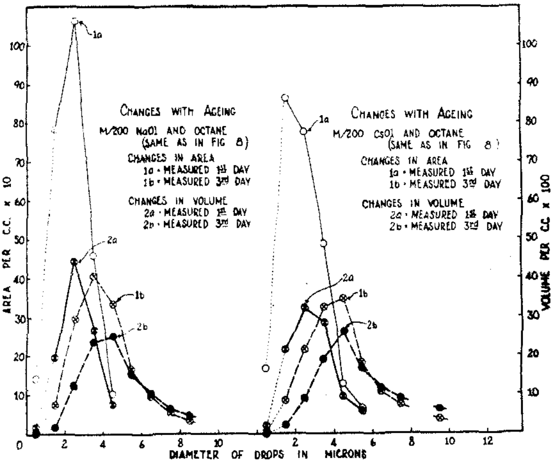


FIG. 7.

centrated emulsions. In general the cream contained about 86 per cent of oil.

Concentrated emulsions were obtained by the use of extremely dilute soap solutions, but 0.008 molal was the greatest dilution which gave an emulsion which was sufficiently stable to measure; that is, to determine the distribution of sizes. Even if every molecule of soap had been present in the interface the area per molecule would have been 190 A^2, or more than nine times the molecular area of oleic acid in its condensed monomolecular film. The actual molecular area was not determined in this case but must have been considerably larger.

The investigation seems in accord with what is given below. The most concentrated emulsion of oil and water thus far produced without the aid of an emulsifying agent is said to contain about 4 percent of oil. However, with soap as an emulsifying agent a highly concentrated emulsion may be obtained by the formation of a *highly dilute monomolecular film*. The film will produce such an emulsion even if it contains only about one-fifth or one-tenth the number of molecules contained in a tightly packed monomolecular film of the soap. Such an emulsion is not stable, and a process occurs in which the distribution of sizes changes in such a way that the mean drop size increases. This causes a decrease in area per molecule until this area becomes about that to be expected for an ordinary tightly packed monomolecular film.

Table 3 gives numbers which are in every case considerably smaller than the actual areas per molecule, since they are calculated on the basis of the assumption that every molecule of soap is in the interface.

TABLE 3.—MOLECULAR AREAS OF INTERFACES BETWEEN DROPLETS OF EMULSIONS.

Emulsions	Minimum (not actual) Molecular Areas × 10^{16} sq. cm. When first made	After 2 days	After 6 days	After 9 days	After 15½ months
M/1200 Na01 and stanolax...	189.9	....	....	....	....
M/200 Na01 and octane......	84.04	48.3	35.6	....	....
M/200 Ca01 and octane......	82.16	45.6	30.3	....	....
M/100 Na01 and octane......	32.41	(24.)	....	18.3	....
M/100 Cs01 and octane.......	32.67	....	....	....	....
M/100 Na01 and octane......	...	....	....	....	12.7

The difference between the minimum and the actual area is indicated by the fact that in the case of the emulsion produced by 0.01 molar sodium oleate only 47.5 per cent of the soap was in the interface, so that the actual area was 50 A^2 instead of 24 A^2. Thus the actual area is always considerably larger than that shown in the table.

In the work described here the area of the interface between the droplets and the continuous phase was determined with great care, but more chemical analyses are essential to exhibit the relations involved.

Griffin [7] and van der Meulen [8] have investigated the question of the molecular area, but have not considered its change with the time. Their work is of considerable interest, but its accuracy depends upon the accuracy with which the distribution of sizes was determined by the microscopic method used. On the whole the number of droplets measured was too small, only about 200 for each curve. In tests of the method of using a drop suspended from a microscope cover glass it was found impossible to secure accurate results.

[7] *J. Am. Chem. Soc.*, 45, 1648 (1923).
[8] Van der Meulen and Rieman, *J. Am. Chem. Soc.*, 46, 876 (1924).

Determination of the Mean Molecular Interfacial Area of an Emulsion.—Measurement of the image produced by a high power microscope was used for the determination of the interfacial molecular area, since, although the work is much more laborious, the method is much more direct than those which involve sedimentation as determined by optical or other methods. These indirect methods are of great use

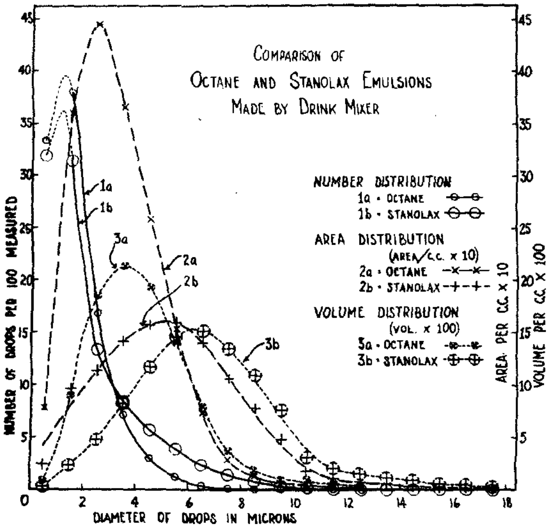


Fig. 8.

in the study of stability, but they give altogether uncertain values of the interfacial area.

Experience indicates that poor results are obtained by the microscope unless considerable attention is paid to the various causes of error.

The method finally adopted was to project the image of thin layer of the emulsion on a specially prepared screen by the use of a powerful arc light and a microscope with 61x, 3mm. apochromatic oil immersion

TABLE 4.—COMBINED NUMBER DISTRIBUTIONS OF EMULSIONS.

Classified according to the type of oil but disregarding the kind of soap and the method of emulsification.

	1 Stanolax Emulsions		2 Octane Emulsions	
Mean Diameter in Microns	Number of Drops	Per cent	Number of Drops	Per cent
0.5	3029	27.56	1889	29.38
1.5	3441	37.30	2296	33.71
2.5	1488	13.54	1161	18.06
3.5	830	7.56	528	8.21
4.5	571	5.19	303	4.71
5.5	378	3.44	116	1.80
6.5	277	2.52	64	1.00
7.5	184	1.67	34	.53
8.5	126	1.15	12	.19
9.5	113	1.03	14	.22
10.5	81	.74	2	.03
11.5	69	.63	5	.08
12.5	72	.66	0	.00
13.5	52	.47	2	.03
14.5	59	.54	0	.00
15.5	33	.30	2	.03
16.5	35	.32	0	.00
17.5	26	.24	1	.02
18.5	25	.23	0	.00
19.5	30	.27		
20.5	17	.15		
21.5	12	.11		
22.5	8	.07		
23.5	9	.08		
24.5	4	.04		
26.5	6	.05		
27.5	6	.05		
28.5	2	.02		
29.5	1	.01		
30.5	1	.01		
31.5	2	.02		
32.5	1	.01		
33.5	0	.00		
34.5	1	.01		
35.5	0	.00		
36.5	0	.00		
37.5	1	.01		
38.5	0	.00		
39.5	0	.00		
40.5	0	.00		
41.5	1	.01		
25.5	1	.01		
	10992	100.00	6429	100.00

objective of 1.40 N.A., and 25x compensating ocular, together with an aplanatic condenser of 1.40 N.A. The magnification was the greatest that could be used profitably, since a high numerical aperture was found essential, and a further increase of magnification decreased too greatly the depth of focus or else lowered the visibility of the smallest droplets.

TABLE 5.—COMBINED EMULSIONS MADE BY DRINK MIXER BUT DISREGARDING THE KIND OF SOAP. (See Figure 8.)

Octane Emulsions

Mean Diameter	Actual No. of Drops	Per cent	No. as Taken from Smoothed Curve	1a Per cent as Taken from Smoothed Curve	2a Sq. Cm. of Area per cc. of Oil × 10⁻³	3a Cc. of Volume per cc. of Oil
0.5	806	33.31	806	33.306	.791	.0099
1.5	918	37.93	918	37.934	3.605	.0901
2.5	408	16.86	408	16.859	4.452	.1855
3.5	171	7.07	171	7.066	3.656	.2133
4.5	73	3.02	73	3.016	2.580	.1935
5.5	29	1.20	29	1.198	1.531	.1404
6.5	10	.41	10	.413	.737	.0799
7.5	2	.08	2.97	.123	.292	.0364
8.5	1	.04	1.08	.045	.136	.0193
9.5	0	.00	.41	.017	.065	.0102
10.5	1	.04	.31	.013	.060	.0104
11.5	1	.04	.16	.007	.037	.0071
12.5	0	.00	.07	.003	.019	.0040
	2420	100.00	2420.00	100.000	17.961	1.0000

Stanolax Emulsions

Mean Diameter	Actual No. of Drops	Per cent	No. as Taken from Smoothed Curve	1b Per cent as Taken from Smoothed Curve	2b Sq. Cm. of Area per cc. of Oil × 10⁻³	3b Cc. of Volume per cc. of Oil
0.5	1283	31.923	1283	31.920	.245	.0031
1.5	1266	31.500	1266	31.500	.969	.0242
2.5	538	13.386	538	13.380	1.144	.0476
3.5	314	7.813	337.6	8.400	1.407	.0821
4.5	242	6.021	227.5	5.660	1.567	.1175
5.5	165	4.105	154.7	3.850	1.592	.1459
6.5	98	2.438	97.6	2.430	1.403	.1520
7.5	68	1.692	56.3	1.400	1.077	.1347
8.5	18	.448	31.7	.790	.779	.1104
9.5	16	.398	15.8	.395	.485	.0768
10.5	4	.100	4.9	.123	.184	.0322
11.5	1	.025	2.4	.062	.108	.0207
12.5	4	.100	1.4	.035	.074	.0165
13.5	0	.000	.9	.023	.056	.0125
14.5	0	.000	.6	.014	.043	.0104
15.5	1	.025	.3	.009	.025	.0063
16.5	1	.025	.2	.005	.019	.0051
17.5	0	.000	.1	.003	.010	.0030
	4019	99.999	4019.0	99.999	11.187	1.0000

The screen was ruled by fine lines about 0.7mm. apart, which corresponded to 1 micron. Since the droplets are in motion, their diameter was estimated when one edge was coincident with one of the lines.

The cell used consisted of a specially designed haemocytometer with a cell 0.1 mm. deep on a slide so thin that it could be used without lowering the efficiency of the oil immersion objective.

Distribution of Sizes in Emulsions.—Figure 8 gives on the x-axis the diameter of the droplets in microns, and on the y-axis (1) the number of drops of diameters between 0 and 1μ, between 1 and 2μ, between 2 and 3μ, etc.; (2) the area $\times$ 10 for each size; and (3) the volume $\times$ 100 for each size.

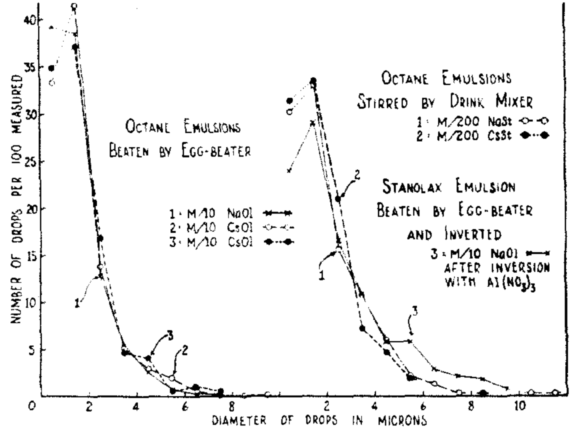


FIG. 9.

To obtain this figure 4019 droplets in stanolax emulsions and 2420 in emulsions of octane were measured. These emulsions were made by the use of 0.1 molar solutions of alkali soap stirred by a high-speed drink mixer. The area per cu. cm. of oil was 11,200 sq. cm. for the emulsion of a heavy paraffin oil (stanolax) and 17,961 for octane. The largest drops had a diameter of 41.5μ with stanolax and 17.5μ with octane.

With an emulsion of octane produced by 0.005 molar sodium oleate the area was 25,500 sq. cm. on the first and 14,630 on the third day, while with caesium oleate the corresponding areas were 24,900 and 13,800, which is an excellent agreement.

The area on the first day for an emulsion of the heavy paraffin oil was 9,600 sq. cm.

Distribution of Sizes and the Nature of the Cation and Anion of the Soap.—The distribution of sizes was found to be the same (Fig. 9) with sodium, potassium or caesium oleate as an emulsifying agent and is thus independent of the atomic volume of the cation. The smaller amount of work done with sodium stearate, elaidate, and cerotate failed to reveal any difference in the curve though the concentrated emulsion with the cerotate exhibited the characteristics of a gel, so the measurements were much less accurate.

With 0.1 *M* potassium chaulmoograte and stanolax, there was a surprising difference. The number of visible droplets of diameters between 0 and 1μ was twice as great as between 1 and 2μ, while with the other anions the number between 1 and 2μ is slightly larger. The emulsions were, however, much less stable and showed more change in a few hours than occurred in a year with emulsions obtained with the same concentration of oleate.

Water-in-Oil Emulsion; *Influence of Metals other than Univalent.*—Magnesium and aluminium oleates were dissolved in stanolax and equal volumes of this oil and water were emulsified. They gave water-in-oil emulsions which, when measured, were found to give number distributions of the same type as those found for oil-in-water emulsions.

A stanolax emulsion produced by 0.1 *M* sodium oleate made in the usual manner was inverted by the addition of the required quantity of aluminium nitrate. The inversion was carried out while beating. When this emulsion was measured it was found to be of the same general type (Curve 3, Fig. 9.) The same procedure was carried out with magnesium nitrate and again an inverted emulsion was the result, but in this case the drops were not spherical but irregular and gave the appearance of being inclosed in solid films. A careful set of measurements was impossible but a rough one was made and the usual distribution of sizes was indicated. These water-in-oil emulsions were not very stable and were almost entirely broken after a week or so.

A large quantity of sodium oleate dissolved in stanolax by warming set to a jelly-like consistency upon cooling. To this solution of sodium oleate in oil was added water, while beating, and a water-in-oil emulsion was formed which broke within a few hours.

Emulsions Made Without a Stabilizing Agent.—It was noticed in the emulsions made with magnesium and aluminium oleates, which were of the water-in-oil type, that the aqueous layers had a very cloudy appearance. When examined under the microscope they were found to contain oil drops, *i.e.*, these aqueous layers were dilute oil-in-water

emulsions. This led to the examination of both layers of an emulsion formed by stirring together equal volumes of stanolax and water without using a stabilizing agent. About two hours after stirring samples were taken from each layer. In the oil layer was found a water-in-oil emulsion and in the water layer an oil-in-water emulsion, but in the latter the concentration of droplets was about ten times greater than in the former. Measurements taken on the drops in these two layers showed number-distribution curves of the usual type except that the curves extended distinctly upward from the 1.5 micron to the 0.5 micron points, there being about 5 per cent more drops of 0.5 micron size than 1.5 micron size in each case.

Viscosity and Distribution of Sizes.—Although the heavy paraffin oil used had nearly two hundred times the viscosity of octane, the surprising fact exhibited by measurements of the droplets is that the peak in the curve of distribution of sizes according to the diameters of the droplets lies at 1.5μ for either oil. The considerable difference which was found is that only one octane droplet of the 6429 measured had a diameter as large as 17.5μ while with the viscous oil the maximum diameter was nearly twice as high (Table V). That other factors than viscosity are involved is shown by the fact that a benzene-in-water emulsion contains more small droplets (peak about 0.5μ) than octane even although the former is somewhat more viscous.

Effect of Acids, Salts, and Bases, and Method of Preparation.—The following additional conclusions were drawn from this work:

1. A number of cases were encountered in which rapid stirring by a motor-driven egg beater failed to emulsify the oil during a period of five minutes, which was not in accord with the usual emulsification in a few seconds. In such cases it was noted that no foam was produced, and that almost at once after a foam was formed the emulsification proceeded in the ordinary way.

2. The method used in preparing an emulsion is one of the factors determining the distribution, but the striking feature of the present work is that the shift of the number maximum is so slight with the different methods of stirring employed.

3. The number distribution of the particles of emulsions stabilized by soaps is changed only slightly by the addition of moderate concentrations of oleic acid or of the corresponding base (as of sodium hydroxide to sodium oleate). However, 0.1 *M* base increased considerably the number of small drops. The stability is, however, usually lessened considerably by the addition, for example, of 0.1 *M* oleic acid to the organic phase, or either 0.1 *M* sodium hydroxide or 0.1 *M* sodium chloride to the aqueous phase before the emulsion is formed.

4. Exceedingly dilute emulsions made *without* stabilizing agents also exhibit the usual type of distribution.

IV. Thickness of the Water Film on Salt Solutions and the Monomolecular Theory

(with Dr. T. F. Young)

In 1917, Langmuir found by the use of inaccurate data that the thickness of the film of water on a potassium chloride solution is independent of the concentration of the salt, and of the order of 3.5 to 4.5 A°. From more accurate values of the surface tensions of salt solutions, Harkins, McLaughlin, and Gilbert,[9] found that the apparent mean

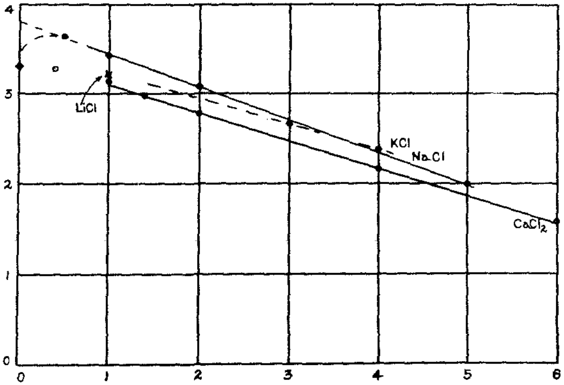


Fig. 10.

thickness of the water film is about 4 A° at 0.1 equivalent concentration of the salt but decreases to about 2 A° at 5.0 *N*. They concluded that the water film corresponds to a monomolecular layer at low concentrations but that as the activity of the salt is increased by an increase of concentration the salt penetrates closer and closer to the surface. Thus at high concentrations of salt the effective thickness of the film is considerably less than the cube root of the volume occupied by a molecule in water (3.1 A°).

While calculations by Goard[10] confirmed these results in concen-

[9] Harkins and McLaughlin, *J. Am. Chem. Soc.*, **47**, 2083 (1925); Harkins and Gilbert, *ibid.*, **48**, 604 (1926).
[10] *J. Chem. Soc.*, **127**, 2451 (1925).

trated solutions, he obtained a much greater thickness in dilute solutions of sodium chloride (6.0 A° at 0.1 *N*). From this Goard and Rideal conclude that the thicknesses are not in accord with the monomolecular theory.

In connection with a critical study of surface tension data undertaken for "International Tables of Critical Constants" the writers have obtained the best information available concerning salt solutions. When combined with the best values now known for the activity coefficients of the salts the thicknesses given in Figure 10 are obtained.

In the case of sodium chloride the best results indicate that the surface tension curve ($\Delta\gamma = (\gamma_{solution} - \gamma_{water})$) is very nearly linear. If it is assumed that it is exactly linear in dilute solutions it is found that the greatest mean thickness of the water film is 3.3 A° which corresponds closely with what should be expected if the film were monomolecular.

The assumption of a linear relation between surface tension and molality below 1.0 molal leads to a maximum in the apparent thickness of the water film at a concentration of about 0.4 molal and a thickness of 3.7 A°. On the whole it seems more reasonable to consider that such a maximum does not exist. If it is assumed that the relation between apparent thickness and molality is linear (upper dotted line, Fig. 10) there must be a slight departure from the linear relation for the surface tension—molality curve, but the departure is so slight that it is impossible by present experimental methods to detect the difference.

On this latter basis the calculated value of the thickness of the water film at zero concentration of sodium chloride (t_0) is 3.8 A°. Thus the film remains essentially monomolecular at extreme dilution of the solution.

V. Thickness of the Water Film Between a Salt Solution and an Organic Phase

(with B. Ginsberg)

The nature of the water film between an aqueous salt solution and an organic phase is of interest in biology. Unfortunately the only information in the literature which has attracted attention indicates that at such an interface salts are positively adsorbed. That this is not true for sodium chloride at the interface between water and benzene is shown by earlier work in this laboratory. The preliminary data obtained in the present investigation show, just as was to be expected, that sodium chloride is negatively adsorbed at such an interface, and that with the more concentrated solutions the thickness of the water

film is almost exactly the same between salt solution and benzene as it is between salt solution and vapor. With dilute solutions, however, the film is slightly thicker with the former than with the latter system.

VI. Monomolecular or Polymolecular Films on Aqueous Solutions of Organic Solutes

(with D. M. Gans)

Are adsorbed films on aqueous solutions of such soluble organic substances as butyl alcohol or nonylic acid one or more molecules in thickness? As yet this question has not been given a definite answer since in calculations in which the adsorption equation has been used to calculate the amount of solute adsorbed, an inexact form of the equation, not that given by Gibbs, has been used. This inexact form of the equation shows that the film is monomolecular with *dilute* solutions provided the activity coefficient for such solutes is not too greatly different from unity. Thus with butyric acid at concentrations between 0.1 and 0.7 molar the area occupied by a molecule of the acid is found as 36 A^2 if the inexact equation $\mu = \frac{1}{iRT} \times \frac{\delta r}{\delta \ln c}$ is used.

The corresponding area for condensed films for palmitic and other insoluble acids of this series is about 19.3 A^2.

The equation of Gibbs may be expressed in an exact form as

$$\mu = \frac{1}{RT} \times \frac{\delta r}{\delta \ln (ma)}$$

in which m is the concentration of solute in moles per 1000 g. of water and a is the activity coefficient. Now if the activity coefficient of butyric acid at 0.66 molal were as low as 40 per cent of the value at 0.1 molal, the area per molecule would be only 18 A^2, or the film might be considered as essentially monomolecular. Any such variation in the activity coefficient is extremely improbable, so the evidence indicates that the film of butyric acid at this concentration is not only merely monomolecular, but in addition is not as tightly packed as palmitic acid in its condensed monomolecular film. Calculations made by the use of the exact form of the equation show that this is true with butyl alcohol. However, calculations made by Mr. Wampler and the writer indicate that in more concentrated solutions the film may be somewhat thicker than monomolecular (in the case of methyl or ethyl alcohol for example).

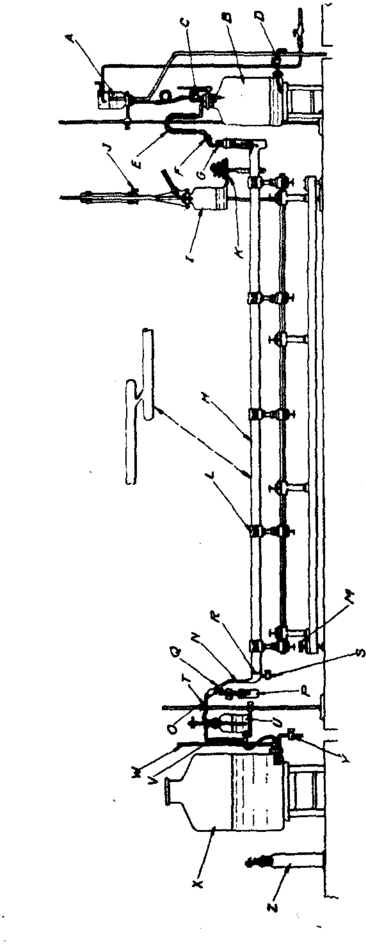


FIG. 11.

The results of Donnan [11] obtained by a direct method indicate an adsorption of nonylic acid about 88 per cent higher than that given by the inexact form of the equation of Gibbs. In this work air was bubbled upward through a vertical tube which contained the solution. The life of each bubble was only about 30 seconds, which should have given too low, and not too high a value as obtained.

According to the recollection of the writer, McBain reported in 1926 some unpublished results obtained with a nearly horizontal tube, which were also very much higher than those given by the inexact common form of the Gibbs equation.

Modification of Donnan's apparatus in which a horizontal tube was applied was designed in this laboratory in 1917, but the work was interrupted before it could be built. Figure 11 shows the apparatus used recently for the direct adsorption of nonylic acid. Preliminary work with this apparatus has given a value for the adsorption equal to 90 per cent of that obtained from surface tension measurements made in this laboratory and from the use of the inexact form of the Gibbs equation. In this work the life of each bubble was 10 minutes. The area per molecule given by the direct method is 36 A^2, but it is known that this is several per cent too high, since a small percentage of the adsorbed material was lost by convection.

The apparatus consists essentially of the nearly horizontal tube H whose straightness may be modified by raising or lowering the clamps L. This allows the speed of the bubbles to be regulated and made what is desired in any part of the length of the tube. On the right is a constant pressure apparatus A to D. At G is a vertical capillary tube which delivers the bubbles. When a bubble is released only the gas in the capillary can expand rapidly, since the clamp F on a rubber tube above the capillary is set with sufficient tightness to prevent a sudden expansion of the gas in the constant pressure system. At R the bubbles enter a glass trap, and then rise up the tube N and break at Q. The height of the bottle I regulates the height of the liquid at Q, and is adjusted by the screw at J. The gas obtained from the bubbles is collected in the bottle U, which is kept at just the pressure of the atmosphere by means of the bottle X. The liquor from the films runs out constantly but slowly into the bottle P. At the completion of the run the concentrations of the liquid in P, and from the trap RNQ (obtained from S), are determined by analytical or surface tension methods.

The newer form of the apparatus has two tubes H, the second higher than the first, with a vertical tube between as shown at HH'. The purpose of this arrangement is to prevent the liquid from which the film has been adsorbed from entering the final trap at R.

[11] *Proc. Roy. Soc.*, (A) 85, 557 (1911).

The most important difference between this apparatus and that of McBain is that in our apparatus the bubble passes into the trap RNQ without any deformation and without any appreciable change of pressure.

VII. The Spreading of Liquids and Antonow's Rule (with B. Ginsberg and H. F. Jordan)

According to Antonow's[1] rule if two liquid phases (A and B) and a vapor phase (C) are in equilibrium the interfacial tension (γ_{AB}) is given by the simple relation

$$\gamma_{AB} = \gamma_A' - \gamma_B'$$

if γ_A' refers to the liquid of higher surface tension. This equation may be written

$$\gamma_A' - (\gamma_B' + \gamma_{AB}) = 0$$

Now the spreading coefficient (S), as defined by the writer, is in this case given by

$$S' = \gamma_A' - (\gamma_B' + \gamma_{AB})$$

Here the primes are used to indicate that mutually saturated phases are considered, so S′ denotes the final or equilibrium value of the spreading coefficient.

Antonow's relation may be restated as follows: For mutually saturated liquids the spreading coefficient is always zero.

Experiments with films of benzene on water indicate that in this case the relation is not strictly true. If the surface of a small body of water is made as clean as possible, benzene will spread over the surface. If the amount of benzene is so chosen as to give a layer about 1 mm. thick, the spreading appears entirely uniform. However, as the benzene evaporates a hole appears somewhere in the layer when the latter has a thickness of about 0.2 mm. The fact that a benzene layer of appreciable thickness remains in equilibrium with the water surface covered with the thin invisible film, indicates that the Antonow relation does not hold even in this favorable case, and that the angle of contact is not zero.

When the phases (including the gaseous phase) were mutually saturated, the ring method with a du Nöuy tensimeter gave the following result for the tension of the invisible film (γ_w'). The other values were obtained by the drop weight method.

$\gamma_w = 72.3$	$\gamma_{w \cdot b} = 34.8$
$\gamma_b = 28.5$	$\gamma_{w \cdot b} + \gamma_b = 63.3$
$\gamma_w' = 62.7$	

[1] *J. Chim. phys.*, 5, 372 (1907).

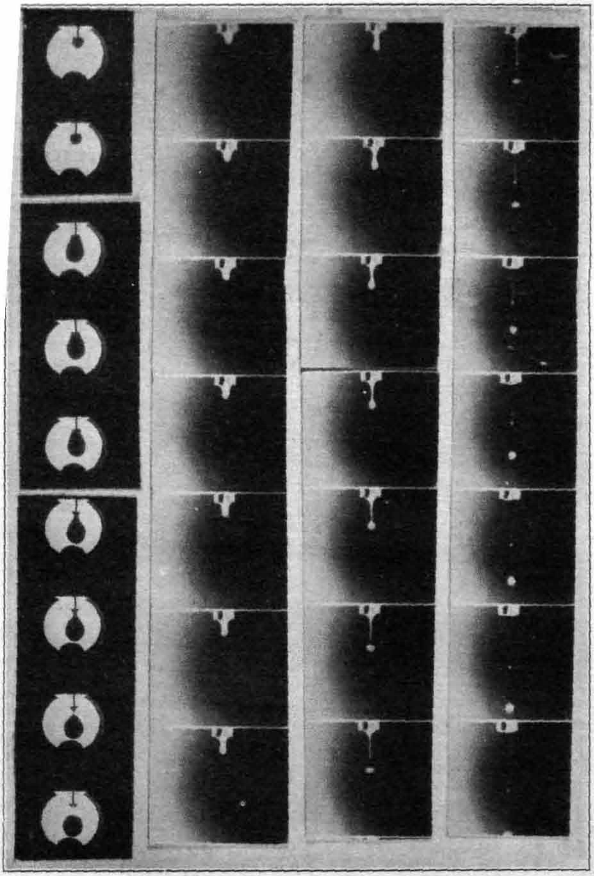


FIG. 12A.—The drops in black are of water falling into an oil of nearly the same density from a narrow tip. The drops in white are of water falling into air from a wide tip. (Speed: black 16 per second; white 128 pictures per second.)

Here w designates water and b, benzene; $\gamma_{w\text{-}b}$ is the tension at the interface and γ_w' represents the tension of the water covered with an invisible film of benzene.

It is apparent that the hole in the layer indicates only that the film of benzene is very thin and not that it is absent.

Can a liquid which does not spread on water, such as carbon disulfide, form a film on the water surface by evaporation and condensation? The surface tension of water at 20° is 72.75 dynes per cm., but in saturated carbon disulfide vapor this was lowered to 70.51. Thus the value of F is 2.24 dynes per cm. The surface tension of carbon disulfide saturated with water is 31.4, so Antonow's relation gives:

$$\gamma_w' - \gamma_{CS_2}' = 70.51 - 31.40 = 39.11 = \gamma_{w'CS_2} \text{ (calculated)}$$

while a measurement by the drop weight method gave 48.36 dynes per cm. Thus with carbon disulfide as well as other non-spreading liquids Antonow's relation, so generally cited as entirely correct, is very far from true.

VIII. The Form of Hanging and Falling Drops

(with B. B. Freud).

Fig. 12 A and B exhibits the form of a few hanging and falling drops. The form of the hanging drop depends upon the value of $\frac{R^3}{V}$, and h, while that of the falling drop may be made to depend upon $\frac{R^3}{V}$ alone, since h may be uniquely determined by the conditions of the experiment. Here R is the radius of the tip; V, the volume of the drop; and h is the height from the bottom of the drop to the level at which the pressure in the column of liquid is the same as that just outside the bottom of the drop. A paper by Professor Freud will present a much more extensive series of motion pictures of falling drops. All of the drops which appear white were taken at the rate of 128 per second, so that all that occurs in the detachment of a drop of water shown in white in Figure 12 A occupied only one-seventh of a second, although the formation of the first of this set of 21 forms was so slow that it required nearly thirty minutes.

IX. The Regional Rule

According to Gibbs the number of phases in a system in equilibrium is given by the relation $P + F = C + 2$. At the interface between any two phases there exists an exceedingly thin layer in which both the

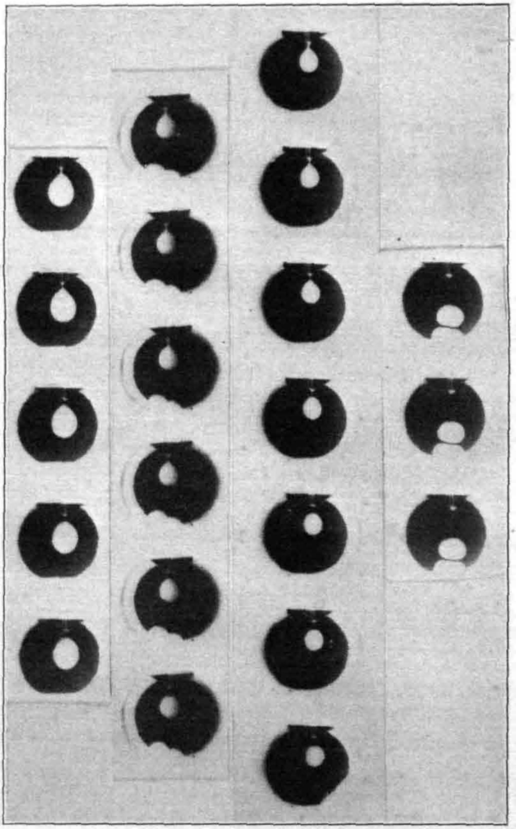
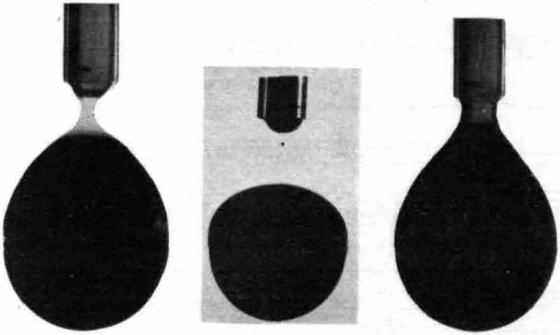


FIG. 12B.—Drops of water falling into an oil of nearly the same density. (Speed: 16 photographs per second.)

properties and the composition are different from what they are in either phase. Such a layer may be designated as an interfacial region, and any phase without the accompanying surface regions may also be considered as a region. Thus if a flask of water is suspended in air, and if the suspension is left out of account, there are three phasal regions—glass, water, and air—and three interfacial regions. If a



D E C

FIG. 12.—The detachment of a drop of orthotoluidin falling into water.

fourth phase, hexane, is added, the number of possible regions is increased to ten, and with five phases to fifteen.

For each interface considered as a region, a new variable is introduced into the phase rule, so

$$R = C - F + I + 2$$

R = number of regions
C = number of components
F = number of degrees of freedom
I = number of interfaces = $R - P$
P = number of phases

The maximum number of regions is

$$R = \frac{C^2}{2} + \frac{5}{2}C - CF - \frac{5}{2}F + \frac{F^2}{2} + 3$$

and the minimum number is

$$R = 2C - 2F + 3$$

Table 6 gives the number of regions, interfaces, and phases for a few systems of zero degrees of freedom.

TABLE 6.—REGIONS, INTERFACES AND PHASES FOR CERTAIN SYSTEMS.

Components (C)	Degrees of Freedom (F)	Phases (P)	Maximum Regions	Maximum Interfaces	Minimum Regions	Minimum Interfaces
1	0	3	6	3	5	2
2	0	4	10	6	7	3
3	0	5	15	10	9	4
4	0	6	21	15	11	5
5	0	7	28	21	13	6

University of Chicago.

ADSORPTION AND CRYSTAL FORM

By Charles H. Saylor

Sodium chloride always crystallizes from pure aqueous solutions in cubes, while in presence of urea we get octahedra or cubes with octahedron faces truncating the corners of the cube. Spangenberg[1] attributes this to the formation of a complex hydrated sodium and urea cation: but this does not explain anything, even if it happens to be true, because it is not a complex salt of urea and sodium chloride which crystallizes.

The most obvious assumption is that urea is adsorbed preferentially on certain crystal faces, thereby changing their rate of growth. However, a direct proof of the preferential adsorption of urea presents enormous analytical difficulties. The problem has been made a general one and has been solved by an indirect method. If we have any substance which can crystallize from aqueous solution in two forms, and we let it crystallize once in presence of a presumably strongly adsorbed cation and the second time in presence of a presumably strongly adsorbed anion, one or the other of the two solutions will show an increased tendency to give the less stable crystal form. As starting solutions we would naturally take acids and bases, or acid and basic dyes. If the less stable form appear, let us say, in alkaline solutions, we can predict that all strongly adsorbed anions will tend to produce the same effect, and that all strongly adsorbed cations will tend to counteract that effect. We can also predict that any substance, like alcohol, which we know decreases the adsorption of anions will tend to decrease the effect of anions. If the presence of urea produces the same change as the presence of strongly adsorbed anions we can predict that addition of alcohol or strongly adsorbed cations will counteract that effect.

It is known experimentally that sodium chloride crystallizes from hydrochloric acid solutions in cubes, just as it does from pure water, while the presence of alkali favors production of octahedron faces. We therefore deduce that the adsorption of anions favors the development of octahedron faces on sodium chloride, and that urea is adsorbed on the same faces that the anions are. It will now be shown that this assumption enables us to predict the effect of many other additions to sodium chloride solutions. It is to be noticed that this new technique is abso-

[1] *Z. Krist.*, 59, 375 (1924).

lutely general and can be applied to any substance crystallizing from any solution or melt. It is not limited to change of habit superimposed upon the same crystal structure, but has already been applied, with some modifications, to the case of calcite and aragonite.

Adsorption, to favor a crystal face, must occur on that face. The flat side of a pea is the side where it has been prevented from growing by nearness to its neighbor. An octahedron, a cube, or any other crystal face is a flat side on the crystal. When adsorption occurs on the eight corners of the cube, the ions of the crystalline substance must first displace the adsorbed material before they can become part of the crystal structure. The filling out of the eight corners is retarded, and eight flat places, the eight faces of the octahedron, develop. Similarly a substance adsorbed along the twelve edges of the cube would cause flat places to develop there. They are the twelve faces of the dodecahedron. In the same way, from the six corners of the octahedron we get the six cube faces, and from the twelve edges, the twelve dodecahedron faces.

We can now predict what the effect upon the crystals of sodium chloride will be when we add many substances to its saturated solution, and also the part of the crystal where adsorption will occur. Urea and readily adsorbed anions are adsorbed on the eight corners of the cube corresponding to the eight octahedron faces. That is why they favor octahedra. Alcohol tends to prevent adsorption of anions, and should decrease the effect of urea and anions. Experimentally we find that it does. From solutions containing alcohol cubes only are formed, the effect of alkali and urea having been neutralized. Organic anions in general are strongly adsorbed. We should therefore expect glycocol to favor octahedra as it does. It is likewise in order that all alkalies produce octahedra. Antimony trichloride in solutions containing hydrochloric acid gives to a certain extent ions of the acid H_3SbCl_6.[2] When sodium chloride is crystallized in the presence of this anion, the ion is strongly adsorbed on the octahedron face and so favors formation of octahedra. So strongly is it adsorbed that when crystals have grown rapidly to large size, the antimony is present as inclusions within the crystal. The inclusions take the form of a milky pyramid opening out fan-wise to the octahedron face. This is conclusive experimental evidence that adsorption occurred on the octahedron face during formation of that face.

As mentioned before, this new technique is absolutely general. It works as well for strongly adsorbed cations as anions. It is not confined in principle to substances crystallizing from solution, but applies equally well to melts. It can be used with substances belonging to any crystal system. Although in any case an adsorbed material may throw the habit either way, a single key reaction makes it possible to predict the

[2] Abegg, "Handbuch der anorganischen Chemie," 3 (III), 589 (1907).

rest. The only condition is that some substance shall be adsorbed preferentially on one of several possible crystal habits.

Take, for example, the case of potash alum. It ordinarily crystallizes in octahedra, but from weakly alkaline solutions, from solutions containing potassium carbonate or borax, it can be crystallized as cubes.[3] Hydroxyl ion is adsorbed not on the octahedron faces of alum, but on the cube faces. We can predict that other anions and urea will also be adsorbed on the cube faces, and will produce cubes. Urea and the only other anion tried, the antimony chloride complex, have that effect.

Barium nitrate crystallizes ordinarily in octahedra,[4] but Gaubert[5] and Walcott[6] have observed that when it is crystallized from solutions containing methylene blue, cube faces develop, and that they are often colored by the dyestuff. Methylene blue is a basic dye and has therefore a strongly adsorbed cation, the color base which by adsorption on the cube face favors that habit. We are enabled, therefore, from this single key reaction to predict what other readily adsorbed substances will do. Barium nitrate shows even from pure water a certain tendency for cube faces to form on the octahedra. We can predict that hydroxyl ion and urea will suppress that tendency, as we find they do. We can further predict that nitric acid will act like methylene blue, the hydrogen ion by adsorption on the cube favoring it. Experiment confirms our prediction. The cube is so strongly favored that crystals grown from acid solution look more like crystals of sodium chloride than barium nitrate. They are cubes with the slightest octahedron truncation. Since in this case it is a strongly adsorbed cation which is effective, we expect alcohol to be without marked effect, as, indeed, experiment shows.

Sodium nitrate crystallizes in the hexagonal system. It is rhombohedral hexagonal. Crystallized from pure water, it forms moderately long six-sided needles with six-sided pyramids at the ends (actually a form of rhombohedra). If we let it crystallize once in the presence of a presumably strongly adsorbed cation, and then in the presence of a presumably strongly adsorbed anion, one should be adsorbed on the pyramids and make short stubby crystals, the prism practically disappearing. The other should be adsorbed on the prism faces producing long thin crystals. Experimentally we find that nitric acid produces this latter effect. From this we can reasonably predict that sodium hydroxide, by adsorption of hydroxyl ion on the pyramid faces will produce the short stubby crystals, which it does.

Negative ions are adsorbed on the octahedron faces of sodium chloride and barium nitrate, on the cube faces of potassium alum, and on

[3] Rinne, "X-Rays and the Fine-Structure of Matter," 136 (1925); Le Blanc, "Crystallotechnic" (1808).

[4] There is a certain doubt as to whether they are really octahedra or ± tetrahedra equally developed, but for our purposes that is immaterial.

[5] "Le Faciès des Cristaux," 13 (1911).

[6] *Am. Mineral.*, 11, 272 (1926).

the pyramids of sodium nitrate. The other principal faces adsorb positive ions. It is reasonable to suppose that, when any of the former crystal faces is rubbed against the other principal faces of the same substance, it will develop a negative charge with respect to those faces which adsorb positive ions. While cases of this kind have not generally been worked out, Vieweg [7] found that an octahedron face of sodium chloride, rubbed against a cube face of the same material, developed a negative charge. Other substances when they are tried will undoubtedly behave in the same way.

Certain modifications must be made in our general method when we apply it to cases where there is a change of crystal structure. There is this essential difference in the two cases. When there is no change of the underlying crystal structure, the *habit* on which adsorption occurs is favored; but when there is a change of structure, the *modification* on which adsorption occurs is repressed. Excessively strong adsorption on a crystal modification tends to peptize it and put each crystal nucleus as it forms into colloidal solution. Consequently it is spoiled as a starting point for crystal growth and supersaturation occurs for want of seed crystals. Thus Marc [8] has shown that quinoline yellow by adsorption on potassium sulfate, prevents crystallization of the sulfate until the solution is greatly supersaturated. Acid dyes cause thallous chloride to supersaturate several hundred per cent. The effect of adsorption in all such cases is to peptize the minute crystals as they form, spoiling them as centers of crystallization. But if the crystalline substance can exist in a metastable modification that is not peptized, there is a strong tendency, when the solution becomes sufficiently concentrated, for the metastable modification to crystallize.

Calcite, under ordinary circumstances, is the only stable modification of calcium carbonate. The numerous and differing forms that appear on calcite correspond to the cube and octahedron of sodium chloride. But aragonite, the orthorhombic modification of calcium carbonate, exists as a mineral in large amounts although it is metastable under all geologic conditions.[9] A third modification of calcium carbonate is metastable under all conditions so far as known. It is hexagonal, optically positive, and variously known as vaterite and μ calcium carbonate.[10] If, controlling all other conditions, we crystallize calcium carbonate once in the presence of a presumably strongly adsorbed cation and once in the presence of a presumably strongly adsorbed anion, one or the other will be adsorbed on the stable form, the calcite. If it is adsorbed strongly enough, it will spoil each calcite nucleus as a center of crystallization instantly it is formed. If it is adsorbed less strongly, it will merely change the shape of the calcite crystals. The latter phenomenon is anal-

[7] Viewig, Cornell University Thesis, "Frictional Electricity," 36 (1924).
[8] *Z. physik. Chem.*, 68, 112 (1910); 73, 708 (1910).
[9] Bäckström, *J. Am. Chem. Soc.*, 47, 2432 (1925).
[10] Johnston, Merwin, and Williamson, *Am. J. Sci.*, 41, 473 (1916).

ogous to adsorption altering the form of sodium chloride. When adsorption is so strong as to prevent growth of recognizable crystals, there is nothing to prevent it being also adsorbed on the metastable modifications of the same substance, altering their form or peptizing them in turn. The effect of adsorption in such examples is capable of greater multiplicity of complications than was dreamed of in the simpler cases first treated.

Crystallize calcium carbonate at 60° C. by adding slowly with stirring 0.1 *M* potassium carbonate to a solution containing a small amount of calcium hydroxide and an excess of potassium hydroxide. Nothing but calcite appears. We change the composition of the medium, adding 0.1 *M* calcium chloride to a solution containing 50 gms. potassium carbonate in 700 cc. of water. We then get principally μ calcium carbonate, with a small amount of aragonite and a trace of calcite. As the amount of carbonate is decreased, aragonite begins to supplant the μ calcium carbonate, and with still smaller amounts calcite replaces the aragonite. Gibson,[11] Wyckoff, and Merwin have varied in this way the amounts of potassium carbonate, and I have checked them in every detail. But, if instead of employing an excess of potassium carbonate, we have an excess of calcium chloride and add carbonate to it, nothing but calcite appears.

I therefore postulate that the carbonate—or more probably the bicarbonate—ion [12] is adsorbed on the calcite, less on the aragonite and least on the μ calcium carbonate, that it peptizes the crystal nuclei of the forms on which it is most strongly adsorbed, and prevents their appearance in recognizable crystals. But those forms on which adsorption of this common ion is less strong can and do crystallize. With decreasing concentration of the ion more and more of the stabler forms appear, first at the expense of the μ form and later at the expense of the aragonite. We have assumed that an anion, HCO_3^-, is adsorbed on the calcite and peptizes it. It is in accord with this assumption that urea and organic anions act in the same way. Urea is known to suppress formation of calcite. When calcium carbonate is crystallized by adding 0.1 *M* potassium carbonate to calcium acetate very few recognizable crystals of calcite are formed. The organic anion is adsorbed on the calcite nuclei and spoils them as centers of crystal growth. If we add alcohol to a solution which would normally allow no calcite to appear, we can now predict that the alcohol will prevent adsorption of anions, and calcite will separate. Adding 0.1 *M* calcium chloride at 60° C. to a solution of 50 gms. potassium carbonate in 700 cc. of water in presence of 5 per cent of alcohol gives about half calcite and half aragonite, although in absence of alcohol it is practically all μ calcium carbonate. Adsorption of anions

[11] *Am. J. Sci.*, 10, 325 (1925).

[12] Becquerel (*Compt. Rend.*, 34, 573 (1852)) left gypsum in contact with a solution of potassium carbonate and in contact with a solution of potassium bicarbonate for about ten years. At the end of that time the gypsum in contact with the carbonate had been replaced by calcite and that in contact with the bicarbonate had been replaced by aragonite.

on the calcite and to a less degree on the aragonite has peptized these forms, and allowed the appearance of another allotropic modification, a form possessing an altogether different structure.

In the course of this paper, a new technique has been worked out which makes it possible to predict the effect of impurities on crystal form. When an added ion alters the form of a substance crystallizing from solution or from a melt, we can predict that a whole group of ions of like charge will do the same. They are adsorbed on the habit they favor. Ions of the opposite charge will stabilize the old habit. The new method makes it possible to deal even with those cases where there is a change of underlying crystal structure. Very strong adsorption on a crystal modification spoils each crystal nucleus and enables metastable modifications to appear. This new technique which resulted from making our problem a general one can be applied to all cases of crystal growth, and through its agency many interesting crystallization problems can be solved.

Cornell University,
Ithaca, N. Y.

ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOAL

By Elroy J. Miller

Because of their relatively great activity, adsorbent charcoals have been used perhaps more frequently than any other adsorbent in studies on adsorption from solution. A review of the literature on the subject of adsorption of electrolytes from solution by charcoal reveals the fact that, with few exceptions, the results of those studies have been largely contradictory and discordant. This is particularly true with regard to adsorption from salt solutions and with regard to the attempts at demonstrating the existence of hydrolytic or decomposition adsorption by a supposedly chemically inert, non-ionogenic adsorbent. In many instances it was recognized that the charcoals used in these investigations were complex and poorly defined substances, but in others it was assumed that they were essentially an amorphous form of carbon and the other constituents were ignored. The great majority of researches on adsorption from solution by charcoal were carried out with blood charcoal, for the reason that it possessed the highest adsorptive capacity of all the available charcoals. Sugar charcoal was used occasionally but usually for the purpose of demonstrating its low activity as compared with that of blood charcoal. Almost without exception the material used was the well-known Merck's blood charcoal. Little or nothing was known about the preparation of this product except that it had been purified by treatment with acids. On burning off the combustihle matter a residue of approximately eight per cent of inorganic matter, or ash, remaineed. In view of these facts it is not surprising, therefore, that in many instances an investigator could not always reproduce his own results.

A summary of the results of the early researches in this field is given elsewhere[1] and only a few of the more recent works will be cited to illustrate the contradictory nature of the results obtained in researches on adsorption from salt solutions which were planned to determine whether or not hydrolytic adsorption existed. The results with the simple inorganic salts were so inconsistent that they were not very generally accepted. The use of acid and basic dyes of the electrolyte type seemed to offer possibilities for the solution of the problem. Since it is a general rule that organic substances are adsorbed more than in-

[1] Bancroft, *J. Phys. Chem.*, **24**, 342 (1920); "Applied Colloid Chemistry," 2nd edition 1926, p. 138 *et seq.*

organic ones, these dyes, with the organic radical in the basic dyes the cation and in the acid dyes the anion, should present ideal conditions for selective adsorption involving hydrolytic splitting. With these ideas in mind, Freundlich and Losev,[2] using crystal violet, a basic dye, found that the organic cation was adsorbed but the chloride anion was left quantitatively in solution. The solution after adsorption was acid. They concluded that the adsorption was hydrolytic. Several years later Freundlich and Neumann[3] re-investigated this adsorption and found that the acid remaining in solution after adsorption of this dye accounted for only a small fraction of the total chloride and the chloride, therefore, was largely in the form of a salt and not hydrochloric acid. It was obvious that ionic exchange with impurities in the charcoal had taken place. Lachs and Michaelis[4] in a study of adsorption from neutral salt solutions, obtained evidence indicating that potassium chloride was hydrolytically adsorbed. They found that after adsorption the chlorine content of the solution had decreased but that the concentration of potassium had remained practically unchanged. They were not able, however, to demonstrate conclusively the presence of potassium hydroxide in the solution after treatment with the charcoal. In 1919 Rona and Michaelis again took up the study of adsorption of electrolytes from solution. From their results with neutral salts and with acid and basic dyes[5] they came to the conclusion that hydrolytic adsorption by charcoal did not take place. Odén and Andersson[6] in 1921 also investigated the adsorption of salts by charcoal and reported that they could find no evidence of hydrolytic adsorption. They expressed the opinion that whenever a solution was acid or alkaline after adsorption the change in reaction was due to the displacement of impurities from the adsorbent and pointed out the fact that an examination of the instances of hydrolytic or decomposition adsorption reported in the literature showed that those adsorbents which are said to adsorb the base and set tbe acid free are derived from acid solutions, or have been treated with acids, whereas the adsorbents which appear to adsorb the acid and set the base free are prepared from alkaline solutions. The change in reaction of neutral salt solutions was attrihuted to the displacement of traces of the acids or bases which had not been removed from the adsorbent.

These conclusions were generally accepted and the theory of hydrolytic adsorption was practically abandoned, even by its former proponents.[7] In view of this situation Bartell and Miller[8] undertook to re-investigate the problem of adsorption from solution, using instead of blood charcoal an activated ash-free sugar charcoal. This charcoal,

[2] *Z. physik. Chem.*, **59**, 284 (1907).
[3] *Z. physik. Chem.*, **67**, 538 (1909).
[4] *Kolloid Z.*, **9**, 275 (1911).
[5] *Biochem. Z.*, **97**, 57 (1919).
[6] *J. Phys. Chem.*, **25**, 311 (1921).
[7] Freundlich, "Kapillarchemie," 3rd edition, 1923, p. 276.
[8] *J. Am. Chem. Soc.*, **44**, 1866 (1922).

prepared by carbonizing pure recrystallized cane sugar and activating at high temperatures in the presence of a limited supply of air, was entirely free from the inherent limitations of blood charcoal. It could be activated until its adsorption capacity equalled or surpassed that of blood charcoal and it thus possessed the necessary adsorptive properties without the complicating factors such as inorganic matter, nitrogen, and the necessity of treatment with acids for purification.

Adsorption of Basic and Acid Dyes.—Adsorption experiments with this ash-free charcoal and solutions of acid dyes and basic dyes indicated that hydrolysis was involved.[8,9] When definite small amounts of solutions of methylene blue and crystal violet were completely decolorized the solutions were strictly neutral and practically no neutral chloride remained in solution. When larger quantities of the solutions were used so that the dye was not completely adsorbed the solutions after adsorption were distinctly acid with hydrochloric acid. From these and other experiments it was evident that hydrochloric acid was set free during adsorption of these basic dyes. When small amounts of the dyes were used both the methylene blue base and the hydrochloric acid were completely adsorbed leaving the solution neutral. When larger quantities of the dyes were used so that the adsorption capacity of the charcoal was no longer capable of adsorbing all the dye, the selective adsorption of the highly adsorbable organic base became manifest and the less adsorbable hydrochloric acid remained in solution.

TABLE 1.—HYDROLYTIC ADSORPTION OF ACID AND BASIC DYES. SUCCESSIVE ADDITIONS OF DYE SOLUTIONS TO CHARCOAL AND AMOUNT OF ACID OR ALKALI SET FREE.

	1st	2nd	3rd	4th	5th	6th	7th	8th
Methylene Blue (0.0025*M*)	16 cc.	16 cc.	16 cc.	16 cc.	16 cc.	16 cc.	16 cc.	16 cc.
(a) CC.N/50 HCl set free..	0.00	0.00	0.00	0.20	0.30	0.40	0.45	
(b) " " " " ..	0.00	0.00	0.00	0.30	0.30	0.40	0.45	0.45
	1st	2nd	3rd	4th	5th	6th		
Sodium Picrate (0.005*M*)	5 cc.	5 cc.	5 cc.	5 cc.	5 cc.	5 cc.		
(a) CC.N/50 NaOH set free	0.95	0.75	0.45	0.25	0.05	0.05		
(b) " " " "	1.00	0.75	0.40	0.25	0.07	0.05		
	1st	2nd	3rd	4th	5th	6th		
Ammonium Picrate (0.005*M*)	5 cc.	5 cc.	5 cc.	5 cc.	5 cc.	5 cc.		
(a) CC.N/50 NH_4OH set free	0.80	0.70	0.40	0.20	0.05	0.05		
(b) " " " "	1.10	0.80	0.60	0.20	0.10	0.05		
	1st	2nd	3rd	4th				
Sodium Eosin (0.0025*M*)	10 cc.	10 cc.	10 cc.	10 cc.				
(a) CC.N/50 NaOH set free	0.75	0.35	0.30	0.20				
Ammonium Eosin (0.0025*M*)	10 cc.	10 cc.	10 cc.	10 cc.				
	1st	2nd	3rd	4th				
(a) CC.N/50 NH_4OH set free	0.70	0.35	0.20	0.15				

With acid dyes such as sodium eosin and sodium picrate quite the opposite effects were observed. The solutions, even when completely decolorized, were distinctly alkaline after adsorption. Data illustrative of the results obtained by Bartell and Miller on the hydrolytic adsorption of acid and basic dyes are given in Table 1. When these changes in reaction were observed it seemed reasonably certain that they were due to hydrolytic adsorption by the charcoal. These effects could not be explained on the hypothesis of adsorbed acids or bases on the adsorbent, for the method of preparation of the charcoal precluded such a possibility. Furthermore, it was difficult to conceive of the displacement of both acid and basic substances from the same charcoal.

Hydrolytic Adsorption of Neutral Salts.—Further evidence that charcoal can cause the reaction of a salt solution to change was obtained when qualitative tests were made on a number of solutions of various

TABLE 2.—CHANGE IN HYDROGEN-ION CONCENTRATION DUE TO ADSORPTION.

Solution	pH Before Adsorption	pH After Adsorption
Sodium chloride	7.0	9.0
Sodium potassium tartrate	7.2	8.6
Sodium citrate	7.8	8.8
Sodium salicylate	7.0	9.4
Sodium acetate	7.2	8.2
Sodium phosphate (Na_3PO_4)	8.2	8.2
Potassium nitrate	6.8	9.4
Potassium chlorate	7.0	8.8
Potassium bromide	7.0	8.6
Potassium iodide	7.0	8.8
Potassium ferrocyanide	7.0	7.8
Potassium phosphate (KH_2PO_4)	4.4	6.6
Ammonium bromide	5.6	8.4
Ammonium chloride	5.6	8.4
Ammonium sulfate	6.8	8.4
Ammonium thiocyanate	5.5	7.8
Ammonium picrate	4.4	8.6
Barium chloride	6.8	8.0
Barium benzoate	7.0	9.0
Barium acetate	7.2	8.+
Calcium acetate	7.4	8.4
Magnesium chloride	6.8	8.0
Magnesium nitrate	6.8	8.0
Lead nitrate	5.0	6.2
Cadmium chloride	6.7	7.4
Manganese sulfate	4.4	7.4
Copper acetate	4.8	4.8
Zinc sulfate	6.8	7.0
Zinc lactate	7.0	7.0
Aluminium sulfate	4.4	4.4
Ferric chloride	4.4	4.4
Mercuric chloride	4.4	3.8
Silver nitrate	6.8	4.4
Silver sulfate	6.8	4.4
Silver acetate	7.+	5.0
Platinic chloride	4.4	4.4
Auric chloride	4.4	4.4

types of salts. The data in Table 2 taken from the second paper by Bartell and Miller [9] show that solutions of salts of bases such as sodium, potassium, ammonium, barium, calcium, and magnesium became more alkaline after treatment with pure charcoal, while solutions of salts of less basic and of noble metals such as aluminum, iron, mercury, silver, gold, and platinum changed little, or became more acid. Salts of the noble metals, silver, gold, and platinum, were reduced to metallic form. From these results it became evident that the pure charcoal adsorbed preferentially the acid and set free the alkali from salts in aqueous solution.

TABLE 3.—ADSORPTION OF ACIDS AND BASES BY CHARCOAL.

Acid or Base	Amount of Acid or Base Adsorbed by 0.25 Gm. of Charcoal Expressed cc. of 0.01 *N* Solution
Group 1. Aromatic Acids.	
Benzoic	75.80
Hydroxybenzoic (salicylic)	73.76
o-Aminobenzoic (anthranilic)	67.00
Group 2. Dicarboxylic Acids.	
Succinic	48.00
Hydroxysuccinic (malic)	35.88
Dihydroxy-succinic (tartaric)	31.76
Aminosuccinic (aspartic)	8.78
Group 3. Aliphatic Acids.	
Formic	15.70
Acetic	16.44
Propionic	24.36
Butyric	35.52
Hydroxypropionic (lactic)	17.86
Amino-acetic (glycocoll)	0.0
Group 4. Inorganic Acids.	
Hydrochloric	11.22
Perchloric	10.86
Nitric	10.08
Sulfuric	9.66
Hydrobromic	8.54
Group 5. Inorganic Hydroxides.	
Sodium	0.10[a]
Potassium	0.00
Calcium	0.00
Barium	0.40[a]
Ammonium	0.00
Magnesium[b]	0.00

[a] These small values are probably due to carbon dioxide.
[b] Nearly saturated solution.

[9] *J. Am. Chem. Soc.*, **45**, 1106 (1923).

Adsorption of Acids and Non-adsorption of Bases by Activated Sugar Charcoal.—In harmony with the fact that the charcoal adsorbed acid and set free alkali from salt solutions was the discovery that the charcoal adsorbed acids from their solutions but did not adsorb the inorganic hydroxides. This is shown in Table 3 which is also taken from the second paper by Bartell and Miller. The evidence thus far obtained indicated quite conclusively that hydrolysis was involved in adsorption from salt solutions. Complete and incontrovertible proof of hydrolytic adsorption became possible when methods were developed for the quantitative removal of adsorbed acids from charcoal.[10] If the alkali liberated in adsorption from salt solution is due to hydrolytic adsorption, then it necessarily follows that an equivalent amount of acid must be adsorbed on the charcoal. The validity of this hypothesis was experimentally verified by means of the methods of estimating adsorbed acids.

TABLE 4.—RECOVERY OF ADSORBED ACIDS FROM CHARCOAL.

Acid	Amount Adsorbed, cc. 0.01 N	Amount Recovered, cc. 0.01 N
Group 1. Aromatic Acids.		
Benzoic	50.30	50.24
	50.30	50.12
Salicylic	50.30	50.18
	50.30	50.30
Group 2. Dicarboxylic Acids.		
Succinic	52.10	52.02
	50.00	49.80
Oxalic	48.10	48.00
	48.10	48.00
Group 3. Aliphatic Acids.		
Acetic	50.30	49.54
	50.30	50.14
Group 4. Inorganic Acids.		
Sulfuric	51.18	50.36
	51.18	51.15
Hydrochloric	50.60	50.26
	20.06	20.02

Quantitative Removal of Adsorbed Acids from Charcoal.—Several methods were developed for the quantitative estimation of adsorbed acids on charcoal. One method, based on the well-known fact that substances are adsorbed less from organic solvents than from water, was found most satisfactory for use with organic acids; the other method, based on the fact that sugar charcoal did not adsorb the inorganic hydroxides, was found most suitable with inorganic acids. The adsorbed organic acids could conveniently be removed from the char-

[10] Miller, *J. Am. Chem. Soc.*, **46**, 1150 (1924).

coal and estimated by shaking a water suspension of the charcoal with an immiscible organic liquid such as benzene or nitrobenzene, and titrating the acid in the water phase with the aid of suitable indicators. The adsorbed inorganic acids could be determined more readily by boiling the charcoal several times with a given amount of standard alkali and titrating the alkali remaining in the filtrates and washings. Results obtained by these methods with charcoal carrying known amounts of adsorbed acid are shown in Table 4. They show definitely that the methods yield quantitative results.

Complete Proof of Hydrolytic Adsorption.—The next step, of course, was to treat solutions of salts with the charcoal, determine the amount of alkali set free, and examine the charcoal for adsorbed acid. The data in Table 5 show the results obtained by the benzene extraction method on charcoal treated with solutions of salts of organic acids. In

TABLE 5.—HYDROLYTIC ADSORPTION OF SALTS OF ORGANIC ACIDS.

Salt	Alkali Set Free During Adsorption from Aqueous Solution (cc. 0.01 *N*)	Acid Extracted from Charcoal After Adsorption (cc. 0.01 *N*)
Sodium benzoate	9.40	9.50
	29.00	28.16
Barium benzoate	9.30	9.30
	3.50	3.50
Sodium salicylate	7.84	7.90
	13.50	13.54
Sodium succinate	6.00	6.12
	2.30	2.20
Potassium oxalate	3.90	3.76
	3.90	3.66
	25.36	25.02
Sodium acetate	7.06	6.90
	3.20	2.80
	1.64	1.78

TABLE 6.—HYDROLYTIC ADSORPTION OF SALTS OF INORGANIC ACIDS.

Salt	Alkali Set Free During Adsorption cc. 0.01 *N*	Acid Extracted from Charcoal After Adsorption, cc. 0.01 *N*	Amount of AgCl or $BaSO_4$ Found in Extract, Equivalent to cc. 0.01 *N* HCl or H_2SO_4
Sodium chloride	11.36	11.33	11.13
	27.42	27.03	27.23
Potassium chloride	13.10	12.90	13.22
	25.86	25.26	25.94
Potassium nitrate	40.54	40.22	....
	25.18	24.67	....
Potassium sulfate	30.58	30.76	30.99
	24.06	23.99	24.37
	26.60	26.91	27.14

Table 6 are the data obtained with salts of inorganic acids by the method of extraction with sodium or potassium hydroxide. In the case of salts such as chlorides and sulfates it was found that the amount of chloride and sulfate removed from the charcoal was exactly equivalent to the amount of acid found on the charcoal. Here, then, was complete proof of hydrolytic adsorption of neutral salts by charcoal. The method of preparation of the charcoal precluded the possibility of attributing the effects to impurities in the adsorbent, the base set free in solution was equivalent to the acid recovered from the charcoal after adsorption, and the acid recovered from the charcoal was the same as that from which the original salt had been derived.

Positive and Negative Adsorption from Salt Solutions.—With the proof of hydrolytic adsorption by charcoal established, it became necessary to determine how much of a factor this might be in adsorption from salt solutions. The fact, mentioned above, that in the adsorption from solutions of inorganic salts such as chlorides and sulfates the amount of chloride or sulfate removed from the charcoal after adsorption was equivalent to the acid adsorbed, suggested that the adsorption

TABLE 7.—ADSORPTION FROM SOLUTIONS OF POTASSIUM SALTS.

Solution	Concentration with Respect to Potassium Before Adsorption	Concentration with Respect to Potassium After Adsorption	Increase or Decrease in Concentration of Potassium	Millimols of KOH Found in Solution After Adsorption
Potassium sulfate	0.019944 *N*	0.020512 *N*	0.000568 *N* +	0.3452
Potassium nitrate	0.019520 *N*	0.020168 *N*	0.000648 *N* +	0.6560
Potassium chloride ...	0.020024 *N*	0.020696 *N*	0.000672 *N* +	0.3846
Potassium oxalate ...	0.020200 *N*	0.021072 *N*	0.000872 *N* +	0.3708
Potassium citrate	0.019680 *N*	0.019768 *N*	0.000088 *N* +	
Potassium benzoate ..	0.019632 *N*	0.009768 *N*	0.009864 *N* —	1.5860
Potassium salicylate ..	0.019608 *N*	0.008568 *N*	0.011040 *N* —	1.5240

in these cases was exclusively hydrolytic. To obtain further evidence on this question the adsorption of a number of potassium salts of organic and inorganic acids was studied. The concentration of the potassium in solution before and after treatment with the charcoal as well as the amount of hydrolytic adsorption was determined. The results presented[11] in Table 7 clearly indicated that adsorption from solutions of the inorganic salts was entirely hydrolytic while that of the salts of the highly adsorbed organic acids such as benzoic and salicylic was partly hydrolytic and partly molecular. The concentration of potassium in solution after adsorption from solutions of the inorganic salts was greater than before adsorption, indicating that negative adsorption of the base took place and that some water was adsorbed along with the acid hydrolytically adsorbed. As stated above the quantity of chloride or

[11] Miller, *J. Am. Chem. Soc.*, 47, 1270 (1925).

sulfate adsorbed was equivalent to the amount of acid adsorbed and to the amount of hydroxide appearing in solution. It is evident from these facts that the adsorption of the potassium ion was negative while that of the anion was positive and that there was no adsorption of these potassium salts as such. The adsorption was exclusively hydrolytic. From these data it can readily he seen why the literature on the adsorption from solutions of these salts by charcoal is contradictory, some investigators reporting positive and others negative adsorptions. The salt solutions after adsorption should be analyzed for both ions of the salt and hydrolytic adsorption should be determined.

Adsorption from solutions of potassium benzoate and salicylate is quite different from the instances just considered. It will be observed that the concentration of potassium after adsorption had decreased to approximately half its original value. It is also evident that the potassium remaining in solution was largely in the form of potassium hydroxide along with a smaller quantity in the form of the potassium salt. The charcoal had adsorbed a large portion of the negative ion as the acid and also a considerable quantity in the form of the potassium salt. Adsorption from these solutions was, therefore, both molecular and hydrolytic in nature.

Negative Adsorption of Bases.—In keeping with the fact that there is an increase in concentration of the base in adsorption from solutions of the inorganic salts is the fact that the strong inorganic

TABLE 8.—EFFECT OF CONCENTRATION ON NEGATIVE ADSORPTION OF POTASSIUM HYDROXIDE.

Concentration of Solution Before Adsorption	Concentration of Solution After Adsorption	Increase in Concentration	Millimols of KOH "Negatively Adsorbed" per Gram of Charcoal
0.005012 *N*	0.005215 *N*	0.000203 *N*	0.0013
0.010104 *N*	0.010486 *N*	0.000382 *N*	0.00212
0.02019 *N*	0.020725 *N*	0.000535 *N*	0.00297
0.03989 *N*	0.040823 *N*	0.000933 *N*	0.00518
0.09960 *N*	0.10114 *N*	0.00154 *N*	0.00855

bases are negatively adsorbed by pure sugar charcoal. Data on the negative adsorption [11] of potassium hydroxide in Table 8 show how this negative adsorption varies with the concentration of the hydroxide. The "negative" adsorption increases with increase in concentration but not proportionally. The amount of water adsorbed decreases with the increase in concentration of the alkali as would be expected from a consideration of osmotic effects. It should be more difficult to adsorb the water from the more concentrated than from the more dilute solutions. Negative adsorption of bases is in striking contrast to the positive adsorption of acids. It agrees very well, however, with the

general behavior of these ash-free charcoals toward acids and bases in attempts to remove them after treatment. When the charcoal has been added to a solution of a base it is a very simple matter to free the charcoal completely from the last traces of that base. Washing once or twice with water removes it quantitatively. With acids it is quite another matter. It is very difficult, if not entirely impossible, to free charcoal from adsorbed acid by the simple process of boiling with water. With pure ash-free charcoal and the methods described for the quantitative removal of adsorbed acids from charcoal it is possible to obtain accurate information on the efficacy of this method of freeing charcoals from acids after treatment. Experiments illustrating this point will be described later. The negative adsorption of bases by charcoal is contrary to the view held by some investigators that negative adsorption by charcoal never occurs in dilute solutions.[12]

Purification of Adsorbent Charcoals and the Properties of the Purified Materials.—*It* has generally been considered that charcoals prepared from various carbonaceous materials have individual and characteristic properties and that, for example, the properties of activated sugar charcoal are peculiar only to charcoal prepared from sugar.[13] This idea was based, partly at least, on work by Ogawa[14] in which charcoals prepared from materials such as sugar, gelatin, and naphthalene appeared to possess individual properties. Subsequently,[15] however, Ogawa found that the differences were not associated with the sources of material from which the charcoals were prepared. From their work with activated sugar charcoal Bartell and Miller,[8, 9] and Miller,[10, 11] had previously pointed out that many of the supposedly characteristic properties of the various charcoals can be explained on the basis of adsorbed substances and occluded, or admixed, inorganic matter. If the supposedly characteristic properties of these charcoals are largely dependent upon the ash and adsorbed substances then it should logically follow that all charcoals would show the same behavior *in adsorption from solutions of acids, bases, and salts as that shown* by the pure sugar charcoal, provided they could be freed from ash and adsorbed material. They should differ only in the magnitude of their activity.

Previous to this time it had not been possible to test this hypothesis experimentally, for there was no method known whereby the inorganic matter could be removed from charcoals. Attempts at extracting the impurities by treatment with concentrated hydrochloric acid[2] and with aqua regia[16] were without success. The ash content of the commonly used blood charcoal could not be reduced much below eight per cent. It

[12] Michaelis, "The Effects of Ions in Colloid Systems," 1925, p. 53.
[13] Michaelis, *op. cit.*, p. 54.
[14] *Biochem. Z.*, 161, 275 (1925).
[15] *Ibid.*, 172, 249 (1926).
[16] Firth and Watson, *Trans. Faraday Soc.*, 19, 601 (1924).

was found,[17] however, that by suitable treatment with hydrofluoric acid the impure charcoals could be freed from ash and inorganic matter. By means of this method adsorbent charcoals of animal, vegetable, and carbohydrate origin may be readily purified so that their ash content is reduced to a few hundredths of a per cent or less. Blood, wood, and impure sugar charcoals when freed from impurities by this method were found to possess the same selective adsorption from solutions of acids, bases, and salts.[18] Their adsorptive properties are identical with those exhibited by the pure activated sugar charcoal. All active, ash- and acid-free charcoals from whatever carbonaceous source prepared, have the same property of adsorbing acids, but not bases. They adsorb certain salts exclusively hydrolytically and certain others partly hydrolytically and partly molecularly. It is useless to compare the activity of such charcoals as blood, animal, wood, and sugar charcoal as has been done in the past, for the activity is not a characteristic property of charcoal from any given source. Charcoals of an equally high order of activity can be prepared from all of these sources. Activated ash-free sugar charcoal, therefore, does not possess unique adsorbent properties characterizing it from other active charcoals.

Experimental Verification of the Causes of the Anomalous Results reported for the Unpurified Charcoals.—The experimental verification of the causes of the anomalous and contradictory results reported in adsorption studies on hydrolytic adsorption and adsorption from salt solutions by unpurified charcoal has been dealt with in detail elsewhere [19] and only a few of the salient points, necessary for a clear understanding of adsorption by ash-free adsorbent charcoal, will be mentioned here. It is certain that the major part of the causes of the contradictory results on hydrolytic adsorption and adsorption from salt solutions was due to the failure to recognize the presence of adsorbed acids and of alkaline and acid impurities in the adsorbent.

Conclusive evidence of this fact has been obtained in two ways: by examination of the unpurified charcoals in the light of the behavior of the purified materials and by reproducing the results with the pure materials to which have been added suitable "impurities" such as adsorbed acids. It was stated above that the charcoal used in the majority of the more recent studies of adsorption from solution was a blood charcoal that had been purified by treatment with acids. Sometimes the material before use was subjected to further treatment for purification by boiling with acid and washing until acid could no longer be detected in the washings. That the adsorbed acid was not all removed by this treatment is certain.

[17] Miller, *J. Phys. Chem.*, 30, 1031 (1926).
[18] Miller, *ibid.*, 30, 1162 (1926).
[19] Miller, *ibid.*, 31, 1197 (1927).

The knowledge of the behavior of activated sugar charcoal toward acids and bases, together with the previously mentioned methods of determining the quantity of adsorbed acid on charcoals, afforded a means of demonstrating the inadequacy of this washing to remove all of the adsorbed acid. An experiment with activated sugar charcoals described by Miller [11] demonstrated this clearly. Two and three-tenths grams of charcoal had adsorbed 0.294 millimol of hydrochloric acid. Extractions with conductivity water at room temperature did not remove the slightest trace of acid. When the charcoal suspension was boiled and filtered while at boiling temperature a small quantity of acid was removed. Fifteen such extractions at boiling temperature removed only half of the acid. The later extractions were removing only traces of acid and it was evident that prolonged extraction would not remove all the acid. Determination of the amount of acid remaining on the charcoal by one of the methods described above, supported by a chloride determination, showed that the other half of the acid was still on the charcoal. Hydrochloric acid is one of the acids least adsorbed and yet the amounts thus irreversibly adsorbed are appreciable and sufficient to alter markedly the behavior of the charcoal. Much larger quantities of the highly adsorbed acids are held in this fashion by active charcoal.

It was pointed out by Bartell and Miller [8] that ash-bearing charcoal becomes alkaline when ignited. Subsequently [19] it was shown that, in addition to adsorbed acids resulting from the extraction with acid, blood charcoal also carries acid material of a complex organic nature resulting from the incomplete decomposition of the organic nitrogenous material in the dried blood. The presence of this complex acid organic matter in the charcoals accounts for the apparent adsorption of bases by many of the unpurified charcoals, for when the charcoal is heated sufficiently high to destroy the organic matter the charcoal loses its power of taking up or neutralizing the inorganic hydroxides.

Further evidence that this is the case is found in the fact that the purified ash-free charcoals when carrying adsorbed organic acids are capable of removing bases from solutions. This is in keeping with the fact that the pure charcoal adsorbs salts of highly adsorbable organic acids partly molecularly. The removal of bases from solution by charcoals carrying adsorbed acids is therefore not a true adsorption of the base but a neutralization by the adsorbed acid with the subsequent adsorption of the salt or, perhaps, strictly speaking, an ionic exchange. When the charcoal carries only adsorbed inorganic acids the action is exclusively one of neutralization of the base without any adsorption of the salt, for the salts of the strong inorganic acids are not molecularly adsorbed. The data in Table 9 picture briefly the effect of heating and the presence of acids on the charcoals on their behavior toward bases.

The results of the adsorption studies with the pure ash-free ad-

TABLE 9.—THE EFFECT OF VARIOUS TREATMENTS ON THE ACTION OF CHARCOALS ON BENZOIC ACID AND SODIUM HYDROXIDE

	Cc. N/50 NaOH Neutralized per Gram of Charcoal	Cc. N/50 Benzoic Acid Adsorbed per Gram of Charcoal
1. Sugar charred below a red heat	14.4	0.0
2. Sugar charcoal heated at 1075° in the absence of air. Not activated	0.0	0.0
3. Sugar charcoal activated at 1075°	0.0	228.0
4. Blood charcoal (as received)	19.0	193.1
5. Blood charcoal (purified) inorganic matter removed and heated at 1075°	0.0	208.8
6. Purified blood charcoal carrying adsorbed methyl red acid	24.4	191.4
7. Purified blood charcoal carrying adsorbed methyl red acid, ignited at 1075° to destroy methyl red acid	0.0	187.0

sorbent charcoals on adsorption from solutions of acids, bases, and salts show a remarkably consistent behavior as compared with the results reported for the unpurified materials. In the light of the results with the pure materials, the anomalous and contradictory findings reported for the impure materials become more intelligible and of additional value because of the information they present on the effects of various substances on the adsorbent action of the activated carbon.

Oriented Adsorption by Adsorbent Charcoal.—It was pointed out by Bartell and Miller [9] that when polar groups such as the hydroxyl and amino groups are introduced into aliphatic and aromatic acids the adsorbability of the resulting substituted acid is lower than that of the unsubstituted acid. An examination of the data on the adsorption of the organic acids listed in Table 3 shows the effect of the hydroxyl and amino groups when introduced into benzoic, succinic, propionic, and acetic acids. The introduction of these groups, in general, decreases the adsorption of the acid to a more or less marked degree, the magnitude of the decrease depending upon the nature of the group and the acid in which it is substituted. The hydroxyl group produces a smaller effect than the amino group. The effect of each group is much more pronounced when substituted in the aliphatic than the aromatic acids. Thus *o*-hydroxybenzoic acid is adsorbed to a slightly less extent than benzoic acid, hydroxysuccinic acid is adsorbed less than succinic acid, dihydroxysuccinic acid is in turn less adsorbed than hydroxysuccinic acid, and hydroxypropionic acid is less adsorbed than propionic acid.

The effect of the amino group is even more pronounced. Orthoaminobenzoic acid is less adsorbed than either benzoic acid or hydroxybenzoic acid. Aminosuccinic acid is very much less adsorbed than suc-

cinic, hydroxysuccinic, or dihydroxysuccinic acids. Aminoacetic acid is not adsorbed at all. This greater effect of the amino group is in accord with the findings of Harkins, Davies, and Clark [20] that the amino group is more polar than the hydroxyl group.

These facts seemed to indicate that an oriented adsorption was being dealt with and that the charcoal plays the same rôle in a charcoal-solution interfacial system that the organic liquid plays in organic liquid-aqueous solution systems and that the Langmuir-Harkins theory of the effect of polar groups applies to adsorption from solution by charcoal. A consideration of a number of other facts of adsorption by ash-free adsorbent charcoals discloses additional evidence in favor of oriented adsorption and the idea expressed by Harkins and co-workers [21] that surface tension phenomena in general are dependent upon the orientation and packing of molecules in surface layers and the forces involved in that action are related to those involved in solution and adsorption. The same facts seem to be in accord with the Gibbs adsorption theorem that those substances which lower the surface tension with increasing concentration are positively adsorbed while those that raise the surface tension with increasing concentration are negatively absorbed. Since there has been no direct method available for the measurement of the interfacial tension of a solid-liquid system there has been no direct way of determining whether the adsorption relationships in the charcoal-solution system are in accord with the Gibbs theorem. It has been considered, however, from grounds based on analogy that the theorem does apply. Freundlich [22] pointed out that the adsorption of the simple fatty acids by blood charcoal increases with their ascending order in the homologous series and that this is in accord with their capillary activity and Traube's rule that the surface tension of their solutions decreases with ascent in the homologous series. Table 3 shows that the adsorption of these acids by ash-free charcoal increases in the same manner. Miller [11] called attention to still other facts in agreement with the Gibbs theorem of surface tension effects. The fact stated above that hydroxysuccinic acid is adsorbed less than succinic acid and dihydroxysuccinic acid is adsorbed less than hydroxysuccinic acid by pure charcoal is in accord with the findings of King and Wampler [23] that the introdution of one and two hydroxyl groups into succinic acid is accompanied by an increased raising of the surface tension of their solutions over that of succinic acid solutions.

Still another fact in striking agreement with the Gibbs adsorption theorem is the negative adsorption of the strong inorganic bases by ash-free charcoal. Theoretically, those substances which raise the surface

[20] *J. Am. Chem. Soc.*, **39**, 541 (1917).
[21] *Ibid.*, **39**, 354 (1917); **39**, 541 (1917).
[22] *Z. physik. Chem.*, **57**, 385 (1907).
[23] *J. Am. Chem. Soc.*, **44**, 1894 (1922).

tension with increasing concentration should be negatively adsorbed. The strong inorganic bases do raise the surface tension and they are negatively adsorbed. Furthermore, in the hydrolytic adsorption of salts the charcoal manifests a selectivity of adsorption of those products of the hydrolysis of salts which lower surface tension and rejects those that raise the surface tension. That is, the acid resulting from hydrolysis is adsorbed and the base is set free.

On the other hand, while these instances make the analogy between adsorption at charcoal-solution interface and adsorption at liquid-liquid and liquid-vapor interfaces more complete, there are other instances that are not in accord with the adsorption theorem. Such an example is the strong positive adsorption of sucrose from solution despite the fact that the surface tension of sucrose solutions is higher than that of water and despite the fact that there are numerous hydroxyl groups that should tend to cut down the adsorption. Possibly in this instance it is the particular arrangement of the hydroxyl groups that nullifies or prevents a polarizing effect. Another possibility, of course, is that the sugar does not raise the interfacial tension of the charcoal-water system as it does the snrface tension of the vapor-water system. It seems likely that the complete solution of the problem will have to await the development of methods for the measurement of solid-liquid interfacial tensions.

Further evidence that the nature and arrangement of groups in the molecule influence the adsorbability is furnished by the data in Table 10. The position of the hydroxyl and amino groups affects markedly the lowering of the adsorption due to the introduction of these groups into benzoic acid. In all three positions the introduction of these groups resulted in a decreased adsorption but the effect was greatest when the groups were in the meta position, least when in the ortho position, and intermediate when in the para position.

The introduction of a second polar group to form sulfosalicylic acid resulted in a still greater lowering of adsorption. Sulfosalicylic acid is very much less adsorbed then benzoic acid or salicylic acid.

The relation of the configuration of the molecule to adsorption is also observable in the adsorption of the aliphatic acids. From the data for the adsorption of butyric, isobutyric, valeric, isovaleric, caproic, and isocaproic acids it is seen that in all three instances the isomeric acid is less adsorbed than the corresponding normal acid. The difference decreases with increase in length of the hydrocarbon chain.

Equally interesting is the effect of the substitution of chlorine in the non-polar end of the acetic acid molecule. In this case the introduction of one chlorine atom increased the adsorption greatly, two chlorine atoms somewhat less, while three chlorine atoms had only a slight effect. Similar results were obtained by Freundlich [22] for these

acids with unpurified blood charcoal. It is significant that both the chlorine atom and hydrochloric acid are adsorbed and that the substitution of the chlorine atom or atoms in acetic acid increases the adsorption rather than decreases it.

Consistent with the adsorption of hydrochloric acid and the favorable effect of the addition or substitution of the chlorine atom on the adsorption of acetic acid is the non-adsorption of the inorganic hydroxides and the decreased adsorption of substances to which have been added the hydroxyl group. It is apparent that certain atoms or groups either consistently favor or consistently oppose adsorption. This supports the contention that the adsorbability of a given substance depends upon the nature and arrangements of the groups or atoms in the molecule. That it is possible to overcome the opposing effect of the hydroxyl group is seen from the fact that the substitution of methyl or ethyl groups for hydrogen atoms in ammonium hydroxide results in an increased adsorption. The data in Table 10 show that ammonium hydroxide is not adsorbed at all, tetramethylammonium hydroxide is very slightly adsorbed, and tetraethylammonium hydroxide is quite appreciably adsorbed.

TABLE 10.—ADSORPTION OF ORGANIC ACIDS AND BASES BY PURIFIED BLOOD CHARCOAL. EFFECT OF ARRANGEMENT OF POLAR AND NON-POLAR GROUPS ON ADSORPTION.

	Cc. 0.01 *M* Acid or Base Adsorbed by 0.25 Gram Charcoal from 100 cc. of Solution
Benzoic acid	73.00
O-hydroxybenzoic acid	71.78
M- " "	61.53
P- " "	65.36
O-aminobenzoic "	68.53
M- " "	57.32
P- " "	65.15
Sulfosalicylic "	56.10
Acetic "	15.68
Chloroacetic "	27.45
Dichloroacetic "	25.54
Trichloroacetic "	17.78
Butyric "	35.39
Isobutyric "	27.42
Valeric "	49.39
Isovaleric "	44.12
Caproic "	62.13
Isocaproic "	59.67
Ammonium hydroxide	0.00
Tetramethylammonium hydroxide	1.20
Tetraethylammonium hydroxide	10.07

Orders of Adsorbability of Salts and Ions.—Numerous researches deal with the determination of the order of adsorbability of

series of salts and of ions by charcoal. Summaries of results of these researches are given by Bancroft.[24] Freundlich,[25] Svedberg,[26] and others, and will, therefore, not be repeated here. It should be pointed out in connection with these researches that blood charcoal was used in all of them and it is, of course, obvious that the usual complicating factors were involved. Ionic exchange with the adsorbed acids and inorganic impurities undoubtedly took place and complicated matters. It was pointed out in a study of adsorption from solutions of a number of potassium salts by pure activated sugar charcoal that hydrolytic adsorption is a factor that must be considered in determining the orders of adsorbability. It is necessary to determine the change in concentration of both ions of a salt remaining in solution after adsorption. In the case of the simple inorganic salts, for example, the adsorption is entirely hydrolytic. Analysis showed that the concentration of the positive ion not only does not decrease, but actually increases while the concentration of the negative ion decreases. This indicates that there is no molecular adsorption of these salts but only adsorption of the acid and liberation of the base. It is obvious that the contradictory reports of the positive and negative adsorption of some of the simple inorganic salts can be accounted for by, and were probably due to, the analysis of the solution for only one or the other of the ions of the salt and to the presence in the charcoal of adsorbed acids and inorganic matter. In some orders of adsorbability potassium hydroxide appears first. In the light of the results with ash-free charcoals it should be last for it is negatively adsorbed.

Adsorbability of Hydrogen and Hydroxyl Ions.—Discrepancies in the reports on orders of adsorbability of ions similar to those appearing for salts are found. They are undoubtedly due to the same causes discussed in the preceding paragraph for salts. The adsorbability of hydrogen and hydroxyl ions is of special importance since these ions have long been attributed with characteristic properties. Hardy [27] was the first to put forth the idea that hydrogen and hydroxyl ions possess certain characteristic properties by virtue of which they play a special rôle in the field of colloid chemistry. Perrin [28] later suggested that because of their abnormal mobility these ions were readily adsorbed and imparted to the adsorbent the charge which they carry. Because the hydroxides seemed to be adsorbed more than their salts the hydroxyl ion was placed first in the order of adsorbability of anions and because acids were adsorbed more than their salts the hydrogen ion was placed first in the order of adsorbability of cations.[29] Rona and Michaelis [30]

[24] "Applied Colloid Chemistry," 1926, 2nd edition, p. 114.
[25] "Kapillarchemie," 3rd edition, 1923, p. 287.
[26] "Colloid Chemistry," 1924, p. 177.
[27] *J. Physiol.*, **29**, 29 (1903).
[28] *J. chim. phys.*, 2, 601 (1904).
[29] Michaelis and Rona, *Biochem. Z.*, **94**, 240 (1919).
[30] *Biochem. Z.*, **97**, 85 (1919).

tried to determine the relative adsorbability of hydrogen and hydroxyl ions by measuring the increase in adsorption of acids and bases caused by the addition of the neutral salts. They concluded that the adsorbability of these ions was of about the same order of magnitude. These conclusions served to strengthen the idea that hydrogen and hydroxyl ions possess similar and unique properties of adsorbability and by virtue of these play a special rôle in colloid chemistry.

When this work was repeated with pure charcoal,[11] however, it it was found that the adsorption of acids was increased by the presence of salts but no alkali was adsorbed from the alkali-salt mixtures. Provided this method of determining the relative adsorbability of the two ions is a valid one, it is obvious that there is no adsorption of the hydroxyl ion while the hydrogen ion is highly adsorbed. In the order of adsorbability of cations the hydrogen ion should be among the highest while the hydroxyl ion should be at the end of the series of anions.

There are other grounds for expecting hydrogen ions and hydroxyl ions to have unlike properties. The fact that the hydrogen ion is the positive electron or proton should lead one to expect it to exhibit inherently characteristic electrical properties and by reason of this fact *per se* it would be unreasonable to expect the hydroxyl ion to have equal and similar properties. These electrical effects in adsorption phenomena should overshadow in importance those of mobility to which Perrin attributed the unusual effects of these ions in colloid systems. But even in the matter of mobility an examination of the facts of adsorption shows that, in general, substances with anions of lower mobility are adsorbed most while those with anions of higher mobilities are adsorbed least. Accordingly, if the mobilities are causal factors and not merely concomitant, then it should follow that the hydroxyl ion should be least adsorbed since it possesses the highest mobility of all the anions. This is in harmony with the fact that potassium hydroxide with its fast moving hydroxyl anion is negatively adsorbed, while potassium benzoate with its slow-moving benzoate anion is positively adsorbed. The same line of reasoning applied to cations would lead to the conclusion that the hydrogen ion is least adsorbed because it is the fastest cation. But from the fact that an acid is adsorbed more than its salts the hydrogen ion is first in the order of adsorbability of cations (excluding some organic cations). Thus both adsorption measurements and consideration of mobility of anions place the hydroxyl ion last in the order of adsorbability of anions. But the mobility considerations do not support the position of the hydrogen ion as determined by the adsorption measurements. There is, however, not as close a correlation of mobility of cations with adsorption as in the case of the anions and it is entirely possible that the mobilities have nothing to do with the adsorbability of ions and are merely concomitant with

the real factors determining adsorbability. Whatever the relative adsorbability of hydrogen and hydroxyl ions may be in other colloid systems the data on adsorption from solutions of acids, bases, and salts by pure charcoal show conclusively that their properties are radically different in charcoal solution systems.

That the hydroxyl group does have special characteristic properties of its own is apparent from other considerations. Langmuir [31] points out the fact that the hydroxyl group does not have any effect on the surface energy of a series of normal saturated aliphatic alcohols. They all have the same surface energy. This effect is explainable on the basis of the energy of the field surrounding the hydroxyl group. The hydrocarbon radicals are arranged in the surface so that the CH_3 groups form the surface while the hydroxyl group is turned toward the bulk of the solution. This is in effect a negative adsorption of that part of the molecule. It was pointed out above that the introduction of the hydroxyl radical into acids invariably cut down the adsorption of those acids by pure charcoal.

It seems, therefore, not merely accidental that the effect of the introduction of the hydroxyl group in organic acids is a decreased adsorption and that the inorganic hydroxides are negatively adsorbed by pure charcoal. The underlying reason is to be sought for in the energy relationships involved in interfacial tension.

The Non-Inversion of Sugar by Adsorbed Acids.—There is much need of information on the properties of substances in the adsorbed state for a better understanding of the phenomena of adsorption, contact catalysis, and reactions at interfaces in general. Michaelis has pointed out [32] that there has been little or no information obtainable from adsorption experiments that can determine whether adsorbed substances are in direct molecular contact with charcoal or only in the superficial layers of water, or whether charcoal acts only to increase the surface of water, or whether as postulated by some,[33] there is a highly concentrated film of solution on the adsorbent and separate from the equilibrium solution.

By the use of ash-free charcoal and by means of the methods for the quantitative estimation of adsorbed acids it has become possible to obtain definite information concerning some of these questions. A consideration of the properties of acids when adsorbed on charcoal reveals a number of significant facts which indicate that the forces with which the acids are held by the charcoal are sufficient to affect profoundly the properties of the acid. Evidence of this is found in the fact that charcoal can adsorb considerable quantities of strong acids so firmly that they cannot be removed by boiling water and the fact that charcoal will adsorb acid hydrolytically from a neutral salt, such

[31] "Colloid Symposium Monograph," vol. 3, p. 50 (1925).
[32] *Op. cit.*, p. 13.
[33] Ostwald and Izaguirre, *Kolloid-Z.*, 30, 279 (1922).

as potassium chloride, even in the presence of hundredth-normal alkali. In order to remove the adsorbed acid quantitatively it is necessary to boil the charcoal several times with an excess of alkali. The significance of these facts becomes more apparent when it is recalled with what avidity the strong acids ordinarily react with the strong bases.

These facts suggest that the adsorption is not simply a concentration of the acid in the water side of the charcoal-solution interface. They do not, however, decide whether or not the acid is in a concentrated solution immediately surrounding the charcoal and separate from the bulk of the solution containing the non-adsorbed hydroxide. Evidence which does seem to decide this question and which affords information of importance for theories of adsorption, catalysis, and reactions at interfaces has been obtained by Miller and Bandemer[84] in a study of the non-inversion of sucrose by adsorbed acids. This evidence proves conclusively that adsorbed acids on ash-free charcoal are incapable of inverting sucrose. With quantities of adsorbed acids sufficiently small so that the adsorption was irreversible at 80° in the presence of five per cent sucrose solution there was no measurable inversion even though there were relatively large amounts of acid and sugar adsorbed. When larger quantities of acid were added to the charcoal so that at 80° in the presence of the five per cent sucrose solution some of the adsorbed acid appeared in solution there was some inversion. The amount of sugar inverted under these conditions was the same as that inverted by an amount of acid and sucrose equivalent to the unadsorbed acid and sugar under the same conditions but in the absence of charcoal. This afforded additional evidence that the ad-

TABLE 11.—NON-INVERSION OF SUCROSE BY ADSORBED ACIDS ON ASH-FREE CHARCOAL

Cc. N/50 Acid Added to 2 Grams of Blood Charcoal	Cc. N/50 Acid in Solution at 80°	Grams of Invert Sugar Found
5.00 hydrochloric	0.00	0.000
5.00 sulfuric	0.00	0.000
5.00 nitric	0.00	0.000
10.00 acetic	0.00	0.000
10.00 stearic	0.00	0.000
10.00 benzoic	0.00	0.000
10.00 salicylic	0.00	0.000
10.00 anthranilic	0.00	0.000
10.00 succinic	0.00	0.000
10.00 malic	0.00	0.000
10.00 tartaric	0.00	0.000
10.00 oxalic	0.00	0.000
39.00 anthranilic	.025	0.04
40.00 salicylic	0.60	0.21
20.00 succinic	1.42	0.08
20.00 malic	1.62	0.17
20.00 tartaric	1.32	0.18

[84] J. Am. Chem. Soc., 49, 1686 (1927).

sorbed acid and sucrose took no part in the inversion. Identical results were obtained with activated sugar charcoal and ash-free blood and wood charcoal with acids of various types, including inorganic, aliphatic, dicarboxylic, and aromatic acids. In Table 11 are presented some of the results obtained with ash-free blood charcoal and a number of acids.

From these facts it seems certain that in the adsorption of substances from solution by solid adsorbents there is not merely a concentration of the substance on the solution side of the interface nor in a highly concentrated film of solution on the adsorbent, separate from the equilibrium solution. If adsorption were of this nature inversion would undoubtedly take place and the inversion might even be expected to be accelerated because of the increased concentration of the reacting substances.

The most reasonable explanation for the nature of the adsorption seems to be that the acid and the sugar are in direct molecular contact with the activated carbon. Since the reaction in this case involves, as one of the reactants, the hydrogen ion and not the undissociated acid, it seems reasonable to conclude that the adsorbed acid on the charcoal is held in the form of undissociated molecules or, possibly, as neutral atoms or groups on the adsorption points of the charcoal lattice.

In view of these facts, the assumption that when acids are adsorbed there exists around the particles of the adsorbent a high concentration of hydrogen ions, seems untenable. Provided that salts are also held in the same manner as the acids (undissociated) it would seem that the facts would be of vital importance for certain theories of surface and membrane equilibria which postulate a higher concentration of ions in the immediate vicinity of the surface.

Non-inversion of sucrose by adsorbed acids on charcoal is apparently an extreme instance of negative catalysis in which both reactants are adsorbed. The possibility that oriented adsorption of either, or both, the acid or sucrose molecules seems precluded, in this case at least, by the fact that the reaction is completely inhibited. If it were merely retarded, orientation, whereby there might arise a tendency to keep the reactive parts of the molecules from coming together, would have to be considered. Furthermore, the orientation of the acids would undoubtedly be with the hydrogen ion away from the charcoal and toward, or in the water phase, for, as pointed out above, the attraction of the charcoal seems to be for the non-polar or hydrocarbon end of the molecule. This orientation with the carboxyl group and the hydrogen ion toward, or in the water or solution phase should favor inversion, provided, of course, the sucrose molecules are not adversely oriented. According to the "diffuse" double layer theory of Gouy [25] the hydrogen ions under these conditions should extend for an appreciable distance into the solu-

[25] *J. Phys.*, 9, 457 (1910).

tion. This should result in inversion. The data in Table 11 show, however, that neither adsorbed inorganic acids nor adsorbed carboxylic acids are able to cause inversion. Thus, considerations of orientation also make it seem reasonable to conclude that the adsorbed acid is in an undissociated state.

That the negative catalysis of the inversion is not due to the strong adsorption of the reaction products with the consequent exclusion of the reactants from the catalyst seems precluded by the fact that glucose and fructose are less adsorbed than sucrose. Experiments designed to test further this point were carried out and it was found that when as little as five milligrams of glucose were adsorbed on two grams of charcoal more than half of it was displaced when the charcoal was suspended in the sugar solution under the usual conditions. It is, therefore, fairly certain that it is not strong adsorption of the products of reaction that inhibits the reaction. On the contrary, it appears that the reactants themselves are so strongly adsorbed that they cannot react.

It was found that the inversion of sucrose by invertase is also completely inhibited when a small amount of invertase is adsorbed on the pure adsorbent charcoal. When larger quantities of invertase were adsorbed the action was not completely stopped although there was no invertase left in solution. In this case, however, conditions are somewhat different, for the invertase is, itself, of colloidal dimensions or associated with particles of colloidal dimensions and it is probable that the charcoal can absorb a certain quantity of invertase in such a condition that it is almost completely surrounded by carbon atoms while larger quantities of invertase are held in such a fashion that the invertase particle comes in contact with charcoal on only part of its surface and leaves the remainder of its surface free to react with sugar molecules coming in contact with it.

There is, therefore, certain evidence that in adsorption from solution by charcoal there is direct contact of the molecules of the adsorbed substance with the adsorbent.

The Buffer Action and So-Called Isoelectric Point of Charcoal.—Considerable attention has been given in recent years to the buffer action of charcoal, chiefly on account of its significance for theories of buffer action in biological processes. Bovie [38] in 1915 reported results showing that charcoal possesses buffer properties. Since that time a number of investigators have shown that, as a rule, an acid solution becomes less acid and an alkaline solution becomes less alkaline upon treatment with charcoal. Attempts have been made to determine by means of electrokinetic methods and by means of buffer solutions the isoelectric point for various charcoals, particularly blood charcoal. As might be expected from the discordant results of the adsorption

[38] *J. Med. Research*, 33, 295 (1915).

studies from solution by blood charcoal the results were, on the whole, not in agreement. As illustrations may be cited the work of Gyemant [37] who found by electrokinetic measurements a pH of 4.0; Umetsu and Michaelis,[38] pH 3.0; Kroetz,[39] pH 7.58; Löffler and Spiro,[40] from results with citrate, borate, and phosphate buffers were unable to assign a definite pH as the isoelectric point although they felt that the buffer effect could not be explained on the basis of impurities. Bohn [41] likewise was not able to assign a definite value for the isoelectric point for all charcoals, and stated that the variations were due to such factors as impurities in the charcoals and the buffer capacity of the solutions employed.

With the hope of finding the causes of the anomalous results Miller and Bandemer [42] undertook an investigation of the subject. From the

TABLE 12.—CHANGE IN pH OF SORENSEN'S PHOSPHATE BUFFER ON TREATMENT WITH CHARCOAL.

pH of Buffer Before Treatment with Charcoal	pH of Buffer After Treatment with Unpurified Blood Charcoal	Ignited Blood Charcoal	Pure Blood Charcoal	Pure Blood Charcoal with Adsorbed Acid
5.3	5.5	6.6	6.2	5.6
6.6	6.6	7.0	6.7	6.4
8.0	7.8	>10.0	9.2	7.0

behavior of pure ash-free charcoal in adsorption from solutions of acids, bases, and salts, and from the behavior of the unpurified blood charcoal and the causes of its anomalous behavior as deduced from the results with the pure charcoal, it seemed probable that the same factors were also operative in the action of the blood charcoal in changing the reaction of the buffer solutions. Since adsorption from buffer mixtures is essentially adsorption from acid-salt and alkali-salt mixtures it was assumed, *a priori*, from the results with pure charcoal in such mixtures, that pure charcoal would not reduce the alkalinity of the alkaline buffers. It was also expected that the pure charcoal when carrying adsorbed acids would reduce the alkalinity and that the blood charcoal, after ignition to drive off adsorbed acids and destroy undecomposed acid organic matter, would not reduce the alkalinity of the alkaline buffers. These expectations were all realized experimentally. In Table 12 are presented some of the data illustrating the results obtained.

With pure charcoal, therefore, there is only the buffering due to the adsorption of acids (and possibly, in some cases, adsorption of salts)

[37] *Kolloid-Z.*, **28**, 103 (1921).
[38] *Biochem. Z.*, **135**, 442 (1922).
[39] *Biochem. Z.*, **153**, 173 (1924).
[40] *Helv. Chim. Acta*, **2**, 417 (1918).
[41] *Biochem. Z.*, **178**, 119 (1926).
[42] Unpublished Research.

from the acid-salt mixtures and to the hydrolytic adsorption of acid from the alkali-salt mixtures of low alkalinity. The alkali-salt mixtures do not become less alkaline when treated with pure charcoal. On the contrary, they become more alkaline, or do not change at all, depending upon the degree of alkalinity.

The isoelectric point for pure charcoal is, of course, non-existent and, strictly speaking, for blood charcoal is fictitious also. At least the reduction of the acidity of the acid solutions is due to a different cause than the reduction of the alkalinity. The former is due to adsorption of acid by the active carbon while the latter is due to interaction of alkali with the acid in the charcoal. From this it may readily be understood that each sample of unpurified charcoal will have different properties depending upon the amount of active carbon and the amount of acid it contains.

Summary and Conclusions

1. Ash-free activated sugar charcoal exhibits the following properties of adsorption from solution: It adsorbs acids but not the inorganic bases. The strong inorganic bases are negatively adsorbed. It adsorbs salts hydrolytically. The adsorption of neutral salts of inorganic acids such as sodium chloride and potassium sulfate is exclusively hydrolytic. Only acid is adsorbed and the corresponding base remains in solution. The adsorption of salts of highly adsorbed organic acids such as sodium benzoate and sodium salicylate is partly hydrolytic and partly molecular.

2. By means of methods for the quantitative removal and estimation of adsorbed acids from ash-free charcoal it has been possible to obtain complete proof of hydrolytic adsorption of salts. This proof is based on the facts that the charcoal is free from impurities, the acid recovered from the charcoal after adsorption is equivalent to the base set free, and the acid is the same as that from which the original salt is derived.

3. Through the development of a method for the purification of adsorbent charcoal it has been demonstrated that all adsorbent charcoals, from whatever source prepared, have the same properties of adsorption from solution after the inorganic matter and acid impurities have been removed. These properties are the same as those possessed by the pure activated sugar charcoal.

4. By treatment of the pure charcoal with suitable substances the anomalous results reported in the literature on adsorption from solution by unpurified charcoal may be reproduced and explained.

5. There is much evidence which indicates that the charcoal plays the same rôle in charcoal-solution interfacial systems that the organic

liquid plays in organic liquid-aqueous solution interfacial systems and that the Langmuir-Harkins theory of the effect of polar groups applies to adsorption from solution by charcoal. The introduction of amino or hydroxyl groups into organic acids invariably results in a decrease in adsorption.

6. It has been pointed out that adsorption by pure charcoal is in closer accord with the Gibbs adsorption theorem than that by the unpurified charcoals.

7. Additional evidence has been presented to show that orientation of molecules is involved in adsorption by charcoal. Thus, the position of the hydroxyl and amino groups in hydroxy and aminobenzoic acids influences markedly the adsorption of these acids. When these groups are in the ortho position the adsorption is greatest, when in the meta position smallest, and when in the para position intermediate. This implies that the adsorption depends largely upon the nature and arrangement of the atoms or groups in the molecule and that certain groups favor and others oppose adsorption. Thus, chloro and dichloroacetic acids are adsorbed much more than acetic acid while aminoacetic acid is not adsorbed at all. Isobutyric acid is less adsorbed than butyric acid, isovaleric acid is less adsorbed than valeric acid, and isocaproic acid is less adsorbed than caproic acid. Ammonium hydroxide is not adsorbed at all. Tetramethylammonium hydroxide is very slightly adsorbed and tetraethylammonium hydroxide is adsorbed as strongly as the inorganic acids. Sulfosalicylic acid is adsorbed much less than benzoic, salicylic, or aminobenzoic acids.

8. Adsorbed acids on charcoal are incapable of inverting sugar. The significance of this fact for certain theories of adsorption and catalysis has been pointed out. It seems certain that adsorbed acids exist in direct molecular contact with the surface atoms of the charcoal. It also seems certain that the adsorbed acids are in an undissociated state. This non-dissociation may explain the fact that acids do not reverse but only decrease the negative charge on charcoal in cataphoresis and electro-endosmosis experiments. The non-dissociation of adsorbed electrolytes on charcoal is of critical importance for theories of electro-kinetic potential.

9. The bearing of the results on the determination of orders of adsorbability of salts and of ions has been pointed out. According to the usual methods of determining the adsorbability of hydrogen and hydroxyl ions by charcoal the results with the pure charcoal indicate that the adsorbability of these ions is not the same but radically different. The hydrogen ion is highly adsorbed but there are a number of facts pointing to the negative adsorption of the hydroxyl ion. The negative adsorption of the hydroxyl ion as determined by adsorption experiments necessitates a revision of the usual explanation for the

fact that charcoal is negatively charged in alkaline solution. Obviously, the negative charge is not due to the adsorption of hydroxyl ions.

10. It has been shown by adsorption from buffer solutions that pure charcoal does not have an isoelectric point and that the isoelectric point for blood charcoal is also fictitious.

Chemical Laboratory,
Michigan Agricultural Experiment Station,
East Lansing, Michigan

SOME UNSOLVED PROBLEMS IN THE MOLECULAR-KINETIC BEHAVIOUR OF COLLOIDAL SUSPENSIONS

By Elmer O. Kraemer

Twenty years ago the attention of some of the leading students of colloid science was being given to the problem of applying to the behaviour of colloidal particles the same molecular-kinetic theory as had been developed to describe the behaviour of gaseous molecules. The theoretical interpretation which Einstein and Smoluchowski gave to the Brownian motion and related effects received a rather extensive experimental confirmation, particularly in the laboratories of Svedberg and Perrin. The same laws, in general, were found to apply to the kinetic behaviour of molecules in ideal gases, solute molecules in ideal dilute solutions, and particles in colloidal suspensions.

One of the theoretical deductions presumably describes to the first approximation the space distribution of a system of molecules or colloidal particles in dynamic equilibrium under the influence of gravity, i.e. the "sedimentation equilibrium." According to the ideal kinetic theory—by which is meant the form of the theory following from the assumption of a negligible volume concentration of uniform spherical particles, the absence of mutual forces between the particles except upon collision, the validity of the appropriate form of Stokes' friction law, and the equipartition of energy principle—the sedimentation equilibrium should be characterized by a logarithmic decrease in concentration n with height h according to the equation

$$\ln n = \ln n_0 - \frac{Nvdg}{RT} h$$

where n_0 equals the number of particles at $h = 0$. Graphically, this ideal case may be expressed, as in Figure 3, by a straight line the slope of which is numerically equal to $\frac{Nvdg}{RT}$, when v is the volume of the spherical molecule or particle, d is its effective density, g is the acceleration of gravity, and the other symbols have their usual significance. These relations may be illustrated more vividly by comparing, as in Table 1, the heights within which the concentration should fall by 99 per cent in various molecular and colloidal systems. Theoretically, the extreme cases present a tremendous difference in the scale of the sedimentation phenomena. As is well known, the vertical distribution of

density in the atmosphere corresponds quite closely to the requirements of the theoretical equation. At the other extreme, practically every book on colloids mentions Perrin's confirmation of the theory within depths of 0.1 mm. in gamboge and mastic suspensions.

Everyday experience, however, appears to be in direct conflict with the theory. Ordinary colloidal suspensions reveal in practice a much greater stability or freedom from sedimentation than corresponds to the simple form of the theory just presented. The literature contains many statements to the effect that colloidal particles may not settle at all. A variety of explanations for this lapse on the part of gravity may be found. Sometimes it is suggested that the phenomenon studied by Perrin is the result of capillary forces limited to an extremely thin surface layer. Frequently, the Brownian motion is supposed to neutralize gravity. Or, at times, repulsive forces between electrically charged particles provide an explanation. One may even find implications of the existence of mysterious protective forces peculiar to the colloidal state or associated with "protective agents" which interfere with the operation of gravity.

TABLE 1.—THEORETICAL SEDIMENTATION EQUILIBRIA AND RATES OF FALL IN VARIOUS DISPERSED SYSTEMS AT 20° C.

Dispersed Phase in H_2O		Radius	Height for 99% Change in n	Rate of Fall
		mμ	cm.	Days per cm.
Gamboge		36	4.7	200.
		100	0.22	26.
	(Barkas)	170	0.045	8.9
	(Costantin)	330	0.0061	2.4
Gold	(Westgren)	20	0.31	7.3
	"	65	0.009	0.7
		100	0.0025	0.3
Silver		5	38.	223.
		10	4.75	56.
	(Barkas)	30	0.18	6.2
	(Burton)	170	0.001	0.2
Copper		5	45.	268.
	(Barkas)	30	0.21	6.6
The Atmosphere			ca 4. × 10^6	

More recent investigations of sedimentation, prompted by this practical stability of suspensions, have led to the conclusion that the ideal kinetic laws for colloidal systems have an extremely limited validity. Such a conclusion is contradictory and inconsistent in a high degree with the earlier work in which practically all ordinary colloidal suspensions susceptible to such studies were ideal in their kinetic behaviour. Although recognizing the necessary limitations to ideal behaviour, the earlier students were able to demonstrate non-ideality in colloidal suspensions to only a very limited extent. The recent investigators, apparently unaware of most of the earlier work, have not com-

pared the new results with the old, and have therefore overlooked the problems and questions which comparison raises concerning the stability and kinetic behaviour of colloidal solutions. Internal evidence suggests that some of the earlier data are fully as reliable as the later; certainly, the later work does not always compare favorably with the earlier from the point of view of the completeness with which relevant data are given.

Whether the results are contradictory in appearance only and may be reconciled by supplementary explanations or whether some of the investigations must be judged faulty and erroneous, it may not be possible to decide without further experimental study. To assist in clarifying the situation, it is desirable that the contradictions be brought out in strong relief and that suggestions be made as to their possible cause. As a starting point, it seems legitimate to accept the results of the simple theory as the limiting or ideal description; inadequacies and discrepancies therefrom may then be expected to appear under certain circumstances with "real" colloidal suspensions as well as with "real" gases. It therefore becomes of importance to ascertain the magnitude and nature of the discrepancies and the conditions under which they arise in order that the kinetic theory of colloidal suspensions may be adequately developed. The purpose of this paper is to survey the evidence which may indicate the limits of validity of the simple kinetic theory, to examine the possible causes for departure from ideal relationships, and to consider particularly the extent to which the electrical charge or the volume of colloidal particles may modify their kinetic behaviour. These questions are basic to the entire subject of stability of colloidal suspensions. In this discussion of them, the major emphasis will be placed upon the experimental facts and relationships.

Brownian Motion under the Influence of a Constant External Force.—In developing the theory of Brownian motion in a gravitational field, Einstein, Smoluchowski, Debye, Schrödinger and their successors assume a uniform gravity drift unmodified by the superposed Brownian motion for colloidal particles suspended in a medium infinitely deep. In other words, after appropriate subtraction of the drift due to gravity from the total motion, the remaining displacements are assumed to be identical with those to be expected in the absence of gravitational influence. This simple additivity relationship was assumed to be approximately true in practical cases during the first stages of sedimentation.

In contrast to this theory, a number of writers explain the stability and absence of sedimentation in colloidal systems by supposing that a sufficiently vigorous Brownian motion overcomes or neutralizes the tendency to settle even in an infinitely deep dispersion, and thereby con-

fers stability on the system.[1] The suggestion that the Brownian motion and gravity fall are not mutually independent is difficult to understand in the absence of some explanation. Theory and experiment indicate the chaotic character of the Brownian motion—particularly the absence of preferred directions of motion. No explanation has been given to show how such a motion should oppose or neutralize the influence of gravity or other external constant force rather than assist it. But the real answer to the question of the superposition of a uniform drift and Brownian motion should be furnished by experiment. Sufficiently careful and detailed observations have been made upon single particles suspended in either gases or liquids. In either case, the external force was due to gravitational or electrical fields.

A series of precise investigations relevant to the question was begun in Millikan's laboratory by Fletcher and continued by Millikan and by Eyring. Fletcher,[2] for instance, utilized observations of the combined Brownian motion and vertical drift (due to gravity or electrical field) of a small particle suspended in a Millikan "electron condenser" to calculate Ne, the faraday, by means of the equation $Ne = \frac{4\,RT}{\pi\,\bar{\Delta}_y^2}\cdot\frac{V + V'}{E}$. $\bar{\Delta}_y^2$ represents the square of the average vertical displacement in one second due to the Brownian motion alone, V equals the velocity of uniform gravity drift and V' equals the velocity of uniform drift under the combined influence of gravity and the electrical field E when the particle carries a single elementary charge. This equation was derived in accordance with the simple form of the kinetic theory upon the assumption that a *single* friction coefficient measures the viscous resistance offered by the medium to the motion of the particle, whether due to Brownian motion, gravity or electrical field, and the assumption that the total motion is equal to the algebraic sum of the motions caused by the various forces if operating separately. Inasmuch as the equation is independent of the friction law, the viscosity of the medium, and the size and density of the particle—quantities not easily determined with precision—Fletcher's investigations offer a particularly effective test of the underlying assumptions. Observations of 1735 displacements yielded a value for Ne of 2.88×10^{14} e.s.u. whereas the accepted value, obtained by electrodeposition of silver, is 2.894×10^{14}. Eyring[3] applied the same

[1] The examples to be found in the following references are typical of such statements:
E. E. Ayres, Jr., in Alexander's "Colloid Chemistry," Vol. I, p. 855.
W. D. Bancroft, "Applied Colloid Chemistry," 2nd ed., p. 171.
W. M. Bayliss, "The Colloidal State," pp. 1, 11.
S. C. Bradford *Biochem. J.*, 15, 553 (1921).
E. F. Burton in Alexander's "Colloid Chemistry," Vol. I, p. 167.
H. N. Holmes, "Laboratory Manual of Colloid Chemistry," p. 62.
Emil Truog, "Colloid Symposium Monograph," 3, 232.
Many other such references could be given containing statements varying in definiteness which indicate the authors' uncertainty concerning the extent to which stability is due to Brownian motion.

[2] H. Fletcher, *Phys. Rev.* (1) 33, 81 (1911).

[3] C. F. Eyring, *Phys. Rev.* (2) 5, 412 (1915).

method to small oil drops suspended in hydrogen; 10,000 observations yielded for *Ne* the value 2.88×10^{14} e.s.u. Since, in many cases, the displacement per second due to the uniform external force was equal in order of magnitude to the mean Brownian displacement per second, the good agreement in the values of *Ne* indicates that even a vigorous Brownian motion does not modify the mean rate of sedimentation of small suspended particles, and therefore does not confer stability greater than theoretical by neutralizing gravity in such systems.

This conclusion was confirmed by the results of another treatment which Fletcher gave his observations. According to the kinetic theory, the square of the average vertical component per second due to Brown-

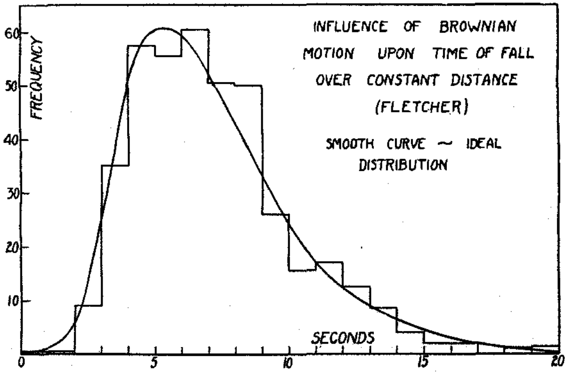


FIG. 1.

ian motion, $\overline{\Delta_y}^2$, is related to the friction coefficient f by the equation $\overline{\Delta_y}^2 = \frac{4}{\pi}\frac{RT}{N}\frac{1}{f}$. Substitution of the empirical values of f and of Δ_y (observed vertical displacement minus the uniform gravity drift) and calculation of N gave the value 5.75×10^{23} instead of the accepted value 6.06×10^{23}. The vigorousness of the Brownian motion for one case is revealed in Figure 1 showing the distribution of the varying times required for a constant vertical fall; the range is between 2 and 25 seconds. But the satisfactory value found for N confirms the assumption that the Brownian motion does not modify the uniform sedimentation of the particle. In a later paper,[4] by essentially the same

[4] H. Fletcher, *Phys. Rev.* (2) 4, 440 (1914).

method, 18,837 observations of combined Brownian motion and gravity fall of particles gave for N the value 6.03×10^{23}.

Finally, Millikan[5] successfully confirmed the kinetic theory of suspended particles showing a still more active Brownian motion by taking advantage of the decreased frictional resistance in gases at low pressures. These careful and detailed investigations appear to leave little room for doubting the independence of the Brownian motion and the rate of gravity sedimentation of an isolated suspended particle under the conditions of these experiments.

The kinetic theory recognizes no fundamental distinction between Brownian motion of particles suspended in a gaseous or a liquid system. If, as suggested by the work just discussed, Brownian motion does not prevent or modify the gravity sedimentation of colloidal particles suspended in a sufficiently deep layer of gas, there seems to be no obvious reason why the same should not also be true of colloidal particles suspended in a liquid. As a matter of fact, the experimental data which are available confirm the assumption of addivity of uniform gravity drift and Brownian motion displacements for liquids as well as gaseous systems, although, it is true, the experiments have not been carried out in such detail or with such precision in the former as in the latter case.

Svedberg and Nordlund[6] developed a method for photographically recording in equal time intervals the combined Brownian motion and gravity sedimentation of ultramicroscopic mercury particles suspended in water. The radii were determined from the mean rate of fall and the Lorentz form of Stokes' law. The vertical displacements due to Brownian motion were obtained by subtracting the mean rate of fall from the observed displacements, in accordance with the assumption of simple superposition of the two. Substitution of these quantities in Einstein's displacement equation allowed the calculation of Avogadro's constant N. Eight hundred and sixty-four displacements yielded a value 5.91×10^{23}, *i.e.* within 2 per cent of the accepted value. In other words, one may infer that, within the limits of experimental error, the Brownian motion of even ultramicroscopic particles does not neutralize gravity sedimentation in the absence of reflection effects from the bottom. Of particular significance is the fact that in all cases the particles were considerably smaller (the radii fell between the limits 119 and 266 mμ.) than the "critical radius" to be discussed below.

Fürth[7] has also studied the influence of gravity upon the Brownian motion of colloidal particles suspended in water by measuring and comparing horizontal and vertical Brownian motion displacements and the uniform gravity drift. An explanation was suggested for the discrepancies sometimes found when the comparison is made in terms of the times of transit over a constant distance, and a tolerable agreement

[5] R. A. Millikan, *Phys. Rev.* (2) 1, 218 (1913).
[6] I. Nordlund, *Z. physik. Chem.*, 87, 40 (1914).
[7] R. Fürth, *Ann. Physik.*, 53, 177 (1917); 59, 409 (1919).

was found in the values of N calculated from the two sets of observations on a single particle.

Another opportunity of examining the influence of the Brownian motion upon sedimentation and stability of colloidal suspensions is provided by some careful data by Westgren[8] comparing the determination of size of particles by methods involving the influence of gravity with the results of independent methods. Table 2 gives a summary of such data with the results depending upon gravity on the left side of the table. Whenever possible, the variation of the single values is indicated; in parenthesis is given the number of values from which each mean is formed. The consistency of the data leads to the inference that the Brownian motion of the particles neither neutralized nor even modified the mean rate of gravity settling. The radius of all particles was less than one quarter the "critical radius" as sometimes defined and said to be non-sedimenting.

These are the principal observations of sufficient detail and precision for the purposes of this discussion. The case may also be mentioned of the atmosphere in which the Brownian motion of the mole-

TABLE 2.—A COMPARISON OF SIZE OF PARTICLE DETERMINATIONS BY VARIOUS METHODS (FROM DATA BY WESTGREN).

Radii in Millimicrons (10^{-7} Cm.)

	Sedimentation Equilibrium	Rate of Micro-sedimentation (Indirect)	Rate of Fall—Stokes' Law	Micro-diffusion	Ultra-microscopic Counting
Se	58.2 ± 0.9 (5)	58.4 ± 5.0 (5)		57.2 ± 1.2 (3)	
Hg	60.0 ± 0.5 (4)	60.5 (1)			
Au	32.8 ± 0.1 (3)	33.4 ± 1.0 (3)		34.5 ± 0.6 (3)	
	40.5 ± 1.6 (5)	42.1 ± 1.6 (3)		42.8 ± 0.3 (3)	
	47.6 ± 0.4 (3)		47.6	51.9 ± 2.0 (3)	
	66.7 ± 0.7 (3)		65.3		
	40.8 ± 0.2 (4)				41.0
	46.8 ± 0.5 (3)				46.7
	53.4 ± 0.9 (4)		53.3		53.5
	65.2 ± 0.1 (2)		65.1		65.3
	32.6 ± 0.1 (3)				32.6
	41.0 ± 0.4 (3)				41.0
	47.1 ± 0.2 (3)		47.2		46.8
	51.9 ± 0.5 (3)		51.8		51.3
	58.9 ± 0.1 (3)		59.0		58.6
	64.9 ± 0.3 (3)		64.5		64.9
				Gilding	
			49.2	49.6 ± 0.2 (3)	49.4 ± 0.6 (4)
			63.8		63.2

[8] A. Westgren, Diss. Upsala 1915; *Arkiv. Mat. Astron. Fysik.*, 11, No. 14 (1916); 13, No. 14 (1918).

cules—in spite of its vigor—does not prevent gravity sedimentation. Altogether, these observations from different laboratories and under a variety of conditions definitely support the assumption made in the kinetic theory that the Brownian motion is simply superimposed upon any uniform drift due to an external force, provided the back diffusion due to concentration gradients is negligible.

The results just surveyed of the direct measurement of Brownian motion, gravity sedimentation, and size of particle furthermore necessitate the abandonment or drastic modification of the current conception of a "critical radius" as a criterion for settling or non-settling. The "critical radius" as defined by equating the Brownian motion displacement per second (as given by Einstein's theoretical equation) with the gravity displacement per second (as given by Stokes' law) [9] may be criticized from both theoretical and practical points of view. Since the mean Brownian motion displacement is proportional to the *square root of the time* interval while the gravity fall is proportional to the *first power of the time*, it is evident that a different value of the "critical radius" corresponds to every different value of the time interval chosen. In the absence of some *a priori* basis for the choice of a suitable time interval, the selection of one second is entirely arbitrary. In addition to the impossibility of defining uniquely the proper time interval, the equating of the two displacements as if they mutually opposed each other is in itself arbitrary. As indicated above, there appears to be just as much justification for adding the mean Brownian motion displacement to the gravity displacement as for subtracting it—whereupon the "critical radius" would lose all possible significance. But of greater cogency is the experimental fact that particles with a much smaller radius than the "critical" value as just defined (*see* Table 3) have been found repeatedly to fall under the influence of gravity in quite a normal manner. The data by Westgren in Table 2 are by no means the only such observations recorded. They simply illustrate some of the most detailed observations made in a careful manner with particles much smaller than the so-called "critical radius." The claim that platinum particles as large as 280 mμ in radius do not settle when suspended in water, is manifestly incorrect. If there really is a "critical radius" sharply separating sedimenting and non-sedimenting particles suspended uniformly in a relatively large system, it must be much smaller than that given by the calculations thus far used. As a corollary,

TABLE 3.—"CRITICAL RADII" FOR VARIOUS PARTICLES SUSPENDED IN WATER (ACCORDING TO BURTON).

Gamboge	Sulfur	Silver	Gold	Platinum
1750 mμ	930 mμ	380 mμ	300 mμ	280 mμ

[9] E. F. Burton in Alexander's "Colloid Chemistry," Vol. 1, p. 167.

other factors must be found to explain the freedom from sedimentation frequently shown by ordinary colloidal suspensions.

Diffusion.—According to Einstein's application of the kinetic theory to diffusion in an ideal colloidal system, the diffusion constant D is related to the radius r of the particles, the viscosity η of the medium, and the temperature by the equation $D = \frac{RT}{N6\pi\eta r}$. If the particles occupy an appreciable volume, or if there are interactions—attractions or repulsions—between the particles, the diffusion coefficient necessarily becomes dependent upon the concentration of the system, and its behaviour becomes non-ideal. If the absence of sedimentation ordinarily observed reflects a volume effect or interaction between particles, this non-ideality should also be displayed in diffusion.

Unfortunately, but a few investigations of diffusion in colloidal systems have been carried out with sufficient care to distinguish between ideal and non-ideal behaviour. The earliest results, obtained by Svedberg[10] are summarized in Tables 4 and 5. The radius calculated by means of Einstein's equation from the data of Table 4 is 0.55 mμ. Although the value for D in Table 4 fluctuates as much as 25 per cent,

TABLE 4.—DIFFUSION OF GOLD PARTICLES IN WATER.

Experiment Number	Layer	Concentration, Particles/cc.	Diffusion Constant
1	1	4.52 × 10[11]	0.26
	2	48.2	0.21
	3	482.	....
	4	920.	0.31
2	1	7.3	0.30
	2	111.	0.35
	3	467.	....
	4	962.	0.24
3	1	7.3	0.28
	2	....	....
	3	350.	....
	4	875.	0.23
	Original	1460. or 19.7 mg./liter.	Average 0.27

no systematic variation with concentration is evident; within the limits of experimental error the systems behaved in an ideal fashion. In spite of the considerable error, the range of concentration in these investigations (300:1) should give rise to a definite drift in the values for D if the cause for the absence of sedimentation in these systems is to be found in interactions between particles or co-volume effects. Similar relationships are indicated by Table 5. The radius calculated

[10] The Svedberg, *Arkiv Kemi Mineral. Geol.*, 3, No. 22 (1909); 4, No. 12 (1911).

TABLE 5.—DIFFUSION OF GOLD PARTICLES IN WATER.

D calculated from the ratio of concentrations in layers 3 and 4.

Experiment number	1	2	3	Average
Diffusion constant	0.123	0.122	0.107	0.117

Original concentration....2.22×10^{14} particles/cc. or 39.4 mg./liter.

from the diffusion data was 1.28 mμ while the value found by the gilding method was 1.33 mμ. These data therefore confirm Einstein's analysis of diffusion of colloids, and lead to the conclusion that the interaction between the particles of sols in even the high concentrations here dealt with is quite insufficient to account for the extreme inconsistency between the theoretical sedimentation equilibrium and qualitative observations of stability.

Interesting investigations of diffusion of colloidal particles on a microscale were carried out by Westgren.[11] After the particles were centrifuged to the bottom of a cell for ultramicroscopic observation, the upward diffusion was followed by direct counts of the number of particles present at various heights and times. The results are summarized in Table 6 and Figure 2. In the table, the ideality of the diffusion is indicated by the agreement between the observed and calculated values of the friction coefficient f. (observed f equals $\frac{RT}{ND}$, calculated f equals $6\pi\eta r$ where r is the radius determined from the rate of sedimentation or from sedimentation equilibrium. In the figure, the ideality of the diffusion is indicated by the straightness of the line connecting the log of the concentration with the square of the corresponding height. The maximum range of height studied was 2.05 mm.

TABLE 6.—A TEST OF EINSTEIN'S EQUATION FOR DIFFUSION OF COLLOIDAL PARTICLES.

Particle	Radius	Concentration Range	f (observed)/f (calc.)
Se	58.2 mμ	1 to 22 $\times 10^{8}$/cc.	0.98 ± 0.02 (3)
Au	32.8 "	1 to 23 "	1.05 ± 0.02 (3)
	40.5 "	1 to 26 "	1.06 ± 0.01 (3)
	47.6 "	1 to 18 "	1.09 ± 0.03 (3)

The measurements by Brillouin[12] of diffusion constants for gamboge particles were made by an indirect and rather unreliable method. Although the results agree only approximately with Einstein's equation, they confirm the conclusions reached above that the non-ideality frequently associated with sedimentation equilibrium in colloidal suspensions is quite inconsistent with the kinetic picture furnished by these other phenomena.

[11] A. Westgren, Diss. Upsala, 1915.
[12] L. Brillouin, *Ann. chim. phys.* (8) 27, 412 (1912).

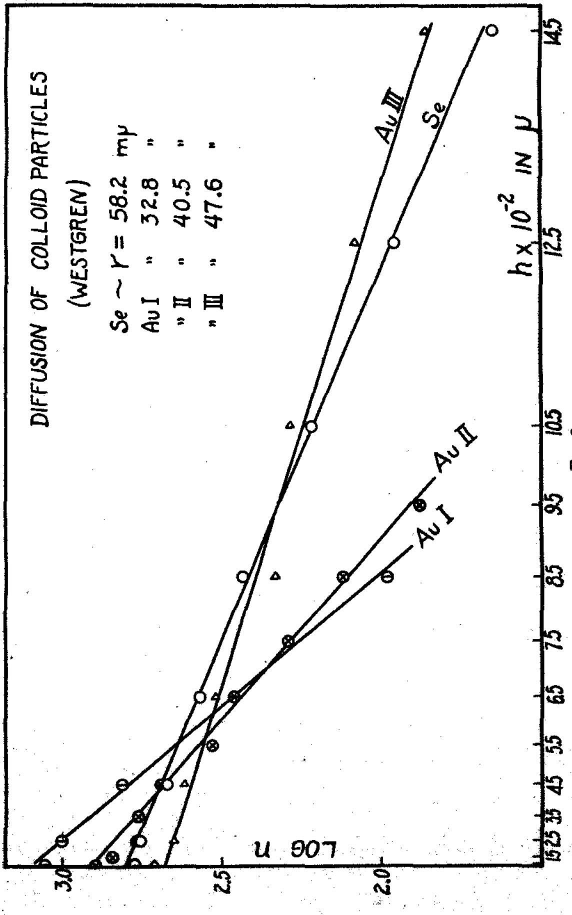

DIFFUSION OF COLLOID PARTICLES
(WESTGREN)
Se ~ r = 58.2 mμ
Au I " 32.8 "
" II " 40.5 "
" III " 47.6 "
Au III
Se
Au II
Au I
LOG n
h x 10^-2 IN μ
3.0
2.5
2.0
1.5
2.5
3.5
4.5
5.5
6.5
7.5
8.5
9.5
10.5
12.5
14.5

FIG. 2.

Spontaneous Fluctuations in Concentration and Osmotic Compressibility.—Probably the most direct manner in which the ideality or non-ideality of a colloidal suspension may be studied is in terms of the "osmotic compressibility." If a microscopic volume of a suspension, bounded optically, be examined, the number of particles within it may be seen to fluctuate spontaneously and continually on either side of the mean value. If the relative degree of the variation with respect to the mean be represented by $\delta \left(= \frac{n - \nu}{\nu}\right)$, the kinetic theory for an ideal system prophesies that the mean value of δ should be given by the equation $\bar{\delta} = 2\, \frac{e^{-\nu} \nu^k}{k!}$, where ν is the mean number of particles in the volume considered and k is the largest integer not exceeding ν. With respect to this phenomenon, the theory recognizes no qualitative distinction between molecules of a gas and colloidal particles. In case the volume of the particles (or molecules) is not negligible, or forces operate between them, the system loses its ideal character, and the spontaneous fluctuations no longer obey the equation just given. The degree of non-ideality may be quantitatively expressed in terms of a factor defined by the equation $\bar{\delta} = 2 \frac{e^{-\nu} \nu^k}{k!} \sqrt{\beta/\beta_0}$. For a gaseous system, β/β_0 equals the ratio of the actual to the ideal compressibility. By analogy, β for a colloidal suspension may be called the "osmotic compressibility," although of course, it does not refer to any actual compressibility of the system in the ordinary sense. Whenever, therefore, experimental determinations of $\bar{\delta}$ yield the value 1 for β/β_0, the colloidal particles behave as an ideal kinetic system, and, in the same range of concentration, should show ideal sedimentation in the absence of external disturbances.

Experimental studies, first by Svedberg[13] (Table 7) and later by Iljin[14] and by Lorenz and Eitel[15] showed that the fluctuations in very dilute colloidal suspensions correspond to the requirements of ideal sys-

TABLE 7.—SPONTANEOUS FLUCTUATION AS A TEST OF IDEALITY IN KINETIC BEHAVIOUR (by SVEDBERG).

Material	Radius mμ	Particles per cc.	Per Cent by Volume	β/β_0
Gamboge	95	4.2×10^8	.0015	0.82
	138	1.4 "	.0015	.93
Gold	19	12. "	.00004	.99
	26	6.1 "	.00004	1.05
	29	3.6 "	.00004	1.02
Mercury	71	1.3 "	.00015	1.13

[13] The Svedberg, "Die Existenz der Moleküle."
[14] B. Iljin, *Z. physik. Chem.*, 83, 592 (1913).
[15] R. Lorenz and W. Eitel, *Z. anorg. Chem.*, 87, 357 (1914).

TABLE 8.—SPONTANEOUS FLUCTUATIONS IN GOLD HYDROSOLS (BY WESTGREN).

Radius mμ	Number of Counts	Particles per cc.	Milligrams per Liter	P/P_0
62.5 mμ	1155	12.7×10^9	250	1.004
	1000	13.4 "	264	0.984
	1447	71.0 "	1400	1.043
	1557	72.5 "	1430	1.009
			Average	1.01
88.5	1021	4.4 "	247	1.009
	1412	5.3 "	297	0.997
	821	6.8 "	381	1.007
	922	12.9 "	723	1.014
	1108	18.3 "	1026	1.083
			Average	1.02
110.0	1351	2.6 "	280	0.993
	1178	4.8 "	516	0.936
	1287	6.0 "	646	1.080
	944	8.0 "	860	0.975
	1084	28.7 "	3090	0.968
	947	30.8 "	3320	0.941
	1310	41.7 "	4487	1.087
	1544	41.7 "	4487	0.976
			Average	0.995

tems, namely $\beta/\beta_0 = 1$. Such investigations were considerably refined and extended by Westgren [16] giving the results summarized in Table 8. These data indicate no appreciable departures from ideal behaviour in these sols having concentrations as high as 72×10^9 particles per cc. or as high as 4.49 grams per liter (0.023% by volume). Since it is inconceivable that discrepancies should arise suddenly or discontinuously, it is likely that even these concentrations could be consider-

TABLE 9.—SPEED OF FLUCTUATIONS IN GOLD HYDROSOLS (BY WESTGREN).

Radius mμ	Number of Counts	Particles per cc.	Milligrams per Liter	P/P^0
46.2	1500	4.4×10^9	35.1	1.03
63.5	1500	0.63 "	13.0	0.99
	1500	0.32 "	6.5	0.96
	1500	0.18 "	3.6	1.11
			Average	1.02
63.5	15000	$0.23–1.25 \times 10^9$	3.0–16.1	$N = 6.09 \times 10^{23}$

ably exceeded before the behaviour of such sols would depart widely from ideal. Departures, therefore, from an ideal sedimentation equilibrium in sols within these concentration limits probably can not be due to volume-of-particle effect, interaction between the particles, or other internal agencies causing non-ideal behaviour.

Westgren also turned his attention to the *speed* of the fluctuations in order to test the ideality of colloidal solutions as kinetic systems. The results are summarized in Table 9. In the first part of the table,

[16] A. Westgren, *Arkiv Mat. Astron. Fysik*, **11**, Nos. 8, 14 (1916); **13**, No. 14 (1918).

the departure from ideality is measured in terms of the ratio of the experimental to the theoretical (for an ideal system) value of a quantity P characterizing the speed of the fluctuations. As may be immediately seen, the systems studied were practically ideal, for P/P_0 approximates 1 in value. In the second part of the table is summarized a painstaking and very extensive series of observations from which, assuming the validity of the ideal equations, Avogadro's constant was calculated to be 6.09×10^{23} in excellent agreement with the accepted value. Here too, it seems unlikely that a moderate extrapolation into greater concentrations should lead to such a degree of non-ideality as would be necessary to give rise to the kind of sedimentation equilibrium claimed to exist by Burton, Porter and other authors.

TABLE 10.—SPONTANEOUS FLUCTUATIONS IN GAMBOGE SOLS (BY COSTANTIN).

Radius	Number of Counts	Particles per cc.	Per Cent by Volume	β/β_0
330 mμ	77	15×10^9	ca. 0.22	1.11
	128	25 "	" 0.38	0.91
	103	33 "	" 0.50	0.91
	54	42 "	" 0.62	0.98
	Data not published for intermediate concentrations			
	104	267×10^9	ca. 4.0	0.62
	114	329 "	" 4.9	0.48
	68	394 "	" 5.9	0.49
	22	450 "	" 6.7	0.40

The only other investigation giving data in sufficient detail to be useful for the purposes of this discussion was made by Costantin [17] on gamboge hydrosols with the results given in Table 10. These suspensions were more concentrated than had hitherto been used. Although the number of counts was too small to give precise results, they show that the departure from ideal behaviour can scarcely exceed 10 percent in concentrations under 0.75 percent by volume. At higher concentrations, as the value of β/β_0 becomes considerably less than 1.0, the failure of the ideal laws in describing the fluctuations becomes unquestionable. In such a case, the kinetic theory of non-ideal systems utilizes the values of β/β_0 in prophesying the nature of the sedimentation equilibrium which should be found in the absence of external disturbances. As will be explained in the next section, Costantin claimed to confirm in this way the sedimentation equilibrium equation for a non-ideal system.

Using the approximate form of van der Waals' equation, $p = \frac{RT}{v} + \frac{bRT - a}{v^2}$, Costantin showed that his values of osmotic compressibility in moderate concentrations could be reconciled with the

[17] R. Costantin, *Ann. phys.*, 3, 101 (1915).

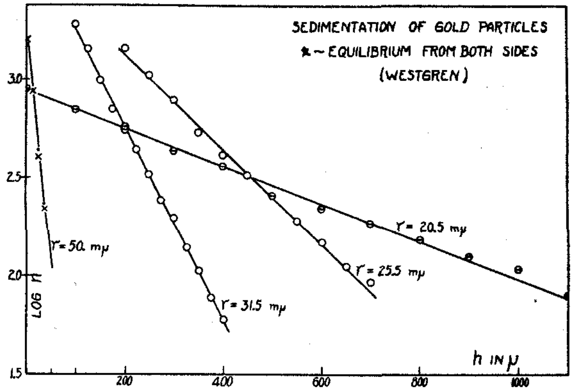

SEDIMENTATION OF GOLD PARTICLES
x ~ EQUILIBRIUM FROM BOTH SIDES
(WESTGREN)
r = 50 mμ
r = 31.5 mμ
r = 25.5 mμ
r = 20.5 mμ
LOG n
h IN μ
3.0
2.5
2.0
1.5
200
400
600
800
1000

FIG. 3.

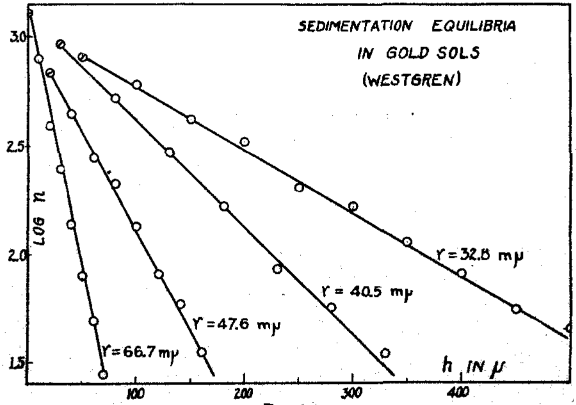

SEDIMENTATION EQUILIBRIA
IN GOLD SOLS
(WESTGREN)
r = 66.7 mμ
r = 47.6 mμ
r = 40.5 mμ
r = 32.8 mμ
LOG n
h IN μ
3.0
2.5
2.0
1.5
100
200
300
400

FIG. 4.

kinetic theory for non-ideal gases by assigning to b a value about twenty times as great as the "true volume" in order to account for the combined influence of the co-volume and the interaction between the particles. This increase in the effective size of the particles, Costantin suggested, corresponds to a negative value of a, i.e. to a repulsive interaction between two particles when they approach each other, or when their electric double layers (according to Gouy's model) tend to interpenetrate upon collision. This equation of state satisfactorily represented the data for concentrations less than 2.5 percent by volume.

In summary, the data on spontaneous fluctuations agree with those on Brownian motion and diffusion in indicating that colloidal sus-

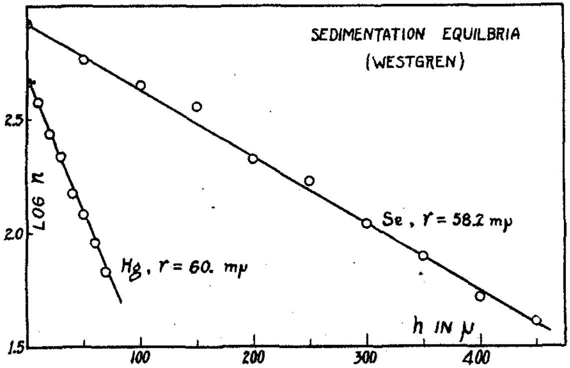


FIG. 5.

pensions in the usual range of concentrations and sizes of particles behave in an ideal manner within the limits of experimental error. It may be suspected that extremely great departures from ideal behaviour in isolated or specific phenomena (as sedimentation equilibrium) reveal a non-ideality due to external rather than internal causes.

Sedimentation Equilibrium.—As is well known, Perrin confirmed the kinetic theory for an ideal sedimentation equilibrium by the examination of gamboge and mastic suspensions over depths not exceeding 0.1 mm. The most extensive study of this phenomenon was that carried out by Westgren.[18] A summary of his most important data is given in Figures 3, 4, and 5 and Table 11.

There are several features of Westgren's work which deserve spe-

[18] A. Westgren, Diss. Upsala, 1915; *Arkiv. Mat. Astron. Fysik*, 9, No. 5 (1913).

cial mention. Sedimentation equilibria were attained from both sides, namely, by settling under the influence of gravity from a state of uniform distribution, and by diffusion against gravity from a state of high concentration near the bottom of the vessel. In both cases, as may be seen in the figures, a logarithmic variation in concentration with height was observed. It is true that in the first series of experiments with the larger particles, the numerical slope of the logarithmic line did not confirm theoretical expectations. This discrenancy, which could not

TABLE 11.—A SUMMARY OF SEDIMENTATION EQUILIBRIA IN VARIOUS HYDROSOLS (BY WESTGREN).

Particle	Radius in mμ	No. of Experiments	Depth Range in mm.	Maximum Concentration		Ratio Max.: Min. Concentration
				Mg./Liter	Particles/cc. $\times 10^{-9}$	
Se	51.5	2	0.45	...	14	16
	58.2	5	.50	99	28	21
Hg	60.0	4	.08	142	14	8
	66.5	1	.10	...	22	27
Au	20.5	1	1.10	19	30	11[a]
	25.5	1	0.50	66	39	15[a]
	31.5	4	.30	79	29	31[a]
	32.6	3	.40	...	9	9[c]
	32.8	3	.50	77	27	18
	40.0	2	.075	...	21	7[a]
	40.5	5	.35	165	31	27
	40.8	4	.26	...	35	22[c]
	41.0	3	.28	...	32	31[a]
	46.8	3	.18	...	37	21[c]
	47.1	3	.16	...	38	19[c]
	47.6	3	.18	199	26	21
	50.0	2	.037	270	28	7[b]
	51.9	3	.14	...	34	31[c]
	53.4	4	.12	...	47	25[c]
	58.9	3	.08	...	37	20[c]
	64.9	3	.08	...	32	35[c]
	65.2	2	.08	...	43	42[c]
	66.7	3	.08	615	26	48

[a] Equilibrium attained by diffusion against gravity. These gave straight log lines but anomalous values of N.
[b] Equilibrium attained from both sides.
[c] Maximum concentration calculation uncertain, but probably the same order of magnitude as values given for particles of the same size. These experiments were in complete agreement with Einstein's equation.

be explained in terms of polydispersity of the suspensions, incomplete attainment of equilibrium, incorrect density of the particles or repulsive forces between the particles, led Westgren to suggest that the equipartition principle may be invalid for large particles—specifically, that the mean kinetic energy of a particle may decrease with increase in size. Subsequent experiments (checked $_c$ in the Table, failed to confirm this interesting suggestion, but, instead, were in complete agreement with Einstein's analysis of sedimentation in an ideal system, giving as a mean value for Avogadro's constant 6.05×10^{23}.

It may also be noted that the depth range considerably exceeded that studied by Perrin and his co-workers. In several cases, the depth was as great as 0.5 mm., and, for the smallest particles, the observations were made over the range of 1.1 mm. without revealing any evidence for appreciable departures from ideal behaviour. Inasmuch as any discrepancy due to either the volume of the particles or to interaction between them would appear gradually, not discontinuously, with increasing depth, Westgren's results suggest that the sedimentation equilibria of particles of the sizes and masses he used should continue practically normal or ideal over depths as much as 100 per cent greater than those studied. The range of depth which could be satisfactorily studied was limited, not by non-ideality of the equilibria, but by the conditions under which accurate ultramicroscopic determinations of concentration could be made: approximately between 1 and 50×10^9 particles per cubic centimeter.

Probably of greater significance than the depth range is the concentration range within which the ideal laws were followed. The maximum volume concentration was in all cases less than 0.005 per cent, which is a high concentration for highly dispersed lyophobic sols. The maximum concentration of about 600 mg. per liter is several times greater than what is sometimes considered a "limiting concentration"[19] for such suspensions. In terms of normality (particles per liter / 6.06×10^{23}), the concentration never exceeded 10^{-10} N corresponding to an ideal osmotic pressure of 5×10^{-12} atmospheres. This concentration is considerably less than that for which spontaneous fluctuations were studied.

The sedimentation equilibrium in a more concentrated system was studied by Costantin, although his data were not published in as great a detail as might be desired. The variation in concentration with height of a gamboge suspension containing particles 330 mμ in radius was determined from photographs of the equilibrium conditions. The data are given in Figure 6. The irregularity in the course of the observed points is probably due to an insufficient number of counts at each level to adequately evaluate the corresponding average concentration. As shown by the straight line representing the limiting law, the sedimentation equilibrium was approximately ideal in concentrations less than 0.8 volume per cent (about 50×10^9 particles/cc.) and within the very small range of 0.02 mm. Above a concentration of 1 per cent, the departure from ideal conditions became more and more pronounced, although no inflection point appeared in the concentration-height curve. If an extrapolation of the curve means anything, it suggests that the increase in concentration with depth would not cease before the particles were almost in actual contact with each other, i.e. when log n equaled 3.37.

[19] E. F. Burton, "The Physical Properties of Colloidal Solutions," p. 87.

Following suggestions previously made by Svedberg, Westgren, and Perrin, Costantin attempted to apply van der Waals' equation of state to his data. In concentrations below 2.4 per cent by volume, this treatment of sedimentation as well as fluctuations data was successful if the combined influence of a and b was represented by a collisional volume about 20 times greater than the actual volume of the particles. As stated in the preceding section, Costantin interpreted this fact in

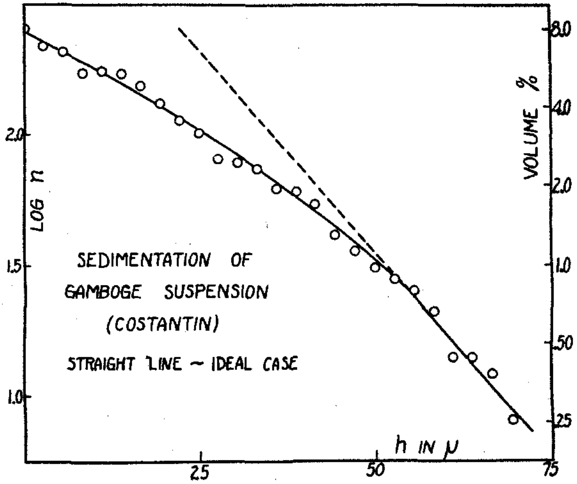


FIG. 6.

terms of repulsive forces arising from the electric double layers surrounding the particles. Although the same equation of state could not adequately reproduce the observations made on more concentrated levels, the sedimentation equilibrium and the spontaneous fluctuations yielded the same values for osmotic compressibility, and therefore lead to the same inferences concerning the operation of repulsive forces between the particles even in the high concentrations. These were the earliest quantitative observations which positively revealed a non-ideal kinetic behaviour in colloidal suspensions.

Thus we see that the investigations before 1920 have consistently indicated ideality in the molecular-kinetic behaviour of the ordinary

dilute colloidal suspensions. In concentrations as high as 0.8 per cent by volume or, in a different case, 10^{15} particles per cc., the various phenomena by which ideality can be tested have shown covolume effects, interaction of the particles and other internal forces to be negligible. Later studies—exclusively of sedimentation—have led to conclusions concerning non-ideality of colloidal suspensions which examination shows to be contradictory to the earlier work. These conclusions should be accepted with a certain reserve, since they have not as yet been confirmed by the investigation of other molecular-kinetic phenomena than sedimentation.

Recognizing, as Svedberg, Perrin, Costantin, Westgren and others had previously done that colloidal suspensions as well as gases need not behave under all circumstances as ideal kinetic systems, Burton [20] and his co-workers have examined macrosedimentation in long columns for the purpose of showing that the concentration of colloidal suspensions is permanently uniform below a very thin layer near the upper surface where the distribution agrees with that of an ideal system.

Gamboge, arsenic trisulfide, Bredig's copper, and Bredig's silver hydrosols were placed in vertical tubes (3.5 × 145 cm.) provided with a number of side-tubes. The tubes were shielded from light and rapid changes in temperature (maximum variation of 7° C.) during a four months period of sedimentation. Samples were then drawn off through the successive side-tubes (*after removal of the sediment*) and analyzed with the following results.

TABLE 12.—SEDIMENTATION IN VARIOUS HYDROSOLS (ACCORDING TO BURTON).

Distance of Side Tube from Upper Surface, in Cm.	Concentration of Sample in Mg. per 50 Cc. Gamboge	As_2S_3	Cu	Ag
8.5	25.7	106.4	3.9	3.3
27.5	26.7	109.5	4.3	3.9
48.5	26.8	104.9	4.3	3.1
69.5	26.5	105.4	4.2	3.6
90.5	27.2	108.0	4.4	3.5
111.5	26.0	106.9	4.3	3.5
132.5	25.6	105.5	4.4	3.3

The failure of the usual kinetic theory to anticipate this low uniform concentration was explained by three hypotheses which do not find expression in the theory ordinarily. First, there is in stable colloidal suspensions a "limiting concentration" which persists in spite of attempts to concentrate by evaporation or otherwise. Second, there is a "critical radius" (as has been discussed above) which defines the maximum size of particles exempt from the operation of gravity.

[20] E. F. Burton and E. Bishop, *Proc. Roy. Soc. London*, **100A**, 414 (1921); E. F. Burton and J. E. Currie, *Phil. Mag.*, **47**, 721 (1924).

Third, the repulsive forces between particles arising as a consequence of the electric double layers preserve a uniform concentration below a certain small depth in spite of gravity. Both the observations and the explanatory propositions deserve some comments.

As was pointed out earlier in the discussion, numerous quantitative observations absolutely prohibit the acceptance of a "critical radius" as at present defined. An acceptable or plausible "critical radius," if there be such, has not yet been defined or demonstrated. Likewise, a "limiting concentration" can be accepted only as a practical limit with respect to certain methods of preparation for certain sols, particularly certain Bredig sols. Reference has been made already in this paper to some of the many suspensions with a stability as great as colloidal suspensions ever have, which have been prepared in concentrations exceeding 0.2 g. per liter. The suggestion of repulsive forces is an interesting one which deserves detailed development. However, it can not be said to have a high degree of usefulness until its introduction into the main body of kinetic theory can yield a series of consequences with respect to diffusion, spontaneous fluctuations, etc., which are in agreement with experiments. Although the idea of repulsive forces is reasonably plausible, very curious and unusual properties must be assigned them if they are to combine with gravity to produce a stable, *uniform* concentration both horizontally and vertically in sols differing in concentration, size, distribution of size, and density of particles.

In connection with Burton's studies, it should be recalled that a troublesome factor in the study of macrosedimentation is the avoidance of temperature gradients which give rise to convection currents interfering with normal settling. The author has frequently observed that a boundary formed by settling in the dark of very small particles (for instance, in gold sols with a particle radius about 50 mμ) may be disturbed by a very short exposure to the light of a low wattage bulb. Mendenhall and Mason [21] have demonstrated the ease with which slight temperature gradients cause convection currents, particularly in suspensions. Barkas [22] has recently described the influence of light upon the sedimentation of fine-grained suspensions which is without doubt partially if not entirely due to temperature gradients. Some uncertainty may therefore be admitted as to whether the temperature changes in the experiments of Burton and Currie took place so slowly that no disturbing convection currents arose.

Perhaps more serious difficulties occur in connection with the sizes, distribution of sizes and densities of the particles in the suspensions, for without these data no comparison can be made between observations and theory. Various types of apparent discrepancy from the theoretical behaviour to be expected with a *uniform* size of particle may arise

[21] C. E. Mendenhall and M. Mason, *Proc. Nat. Acad. Sci.*, 9, 199, 202 (1923).
[22] W. W. Barkas, *Phil. Mag.*, 2, 1019 (1926).

solely because of polydispersity of the suspension. Because of the complexity which polydispersity introduces into the theoretical treatment, it is not feasible to use other than uniform sized particles in testing the validity of the ideal kinetic laws. In practically all cases, it is necessary to use some artifice—fractional coagulation, fractional sedimentation or special methods of preparation, as gilding of gold nuclei—in order to obtain suitable material for studies of molecular-kinetic behaviour. Since Burton and his co-workers give no information concerning the dispersity of their material and make no mention of any fractional procedures, their suspensions were presumably polydisperse. Such ill-defined material can not be expected to serve well in establishing the limits of validity of the ideal kinetic theory.

As a guide in estimating the conditions whch may have existed in Burton's sedimentation tubes, Stokes' law for the rate of fall of suspended particles under conditions far from equilibrium may appropriately be used. The data summarized or referred to in the earlier part of this discussion, it is suggested, so directly deny the existence of a "critical radius" greater than 25-100 mμ, or a real "limiting concentration" as low as a few tenths grams per liter, and so positively confirm Stokes' law for falling particles in spite of their Brownian motion that the writer prefers to explain the few anomalous cases of sedimentation in simple terms—at least until it is shown that every aspect of the kinetic behaviour of suspensions unanimously requires a group of new hypotheses.

As a consequence of accepting Stokes' law and of assuming that Burton and Currie's temperature control was adequate, the approximately uniform concentration observed after sedimentation leads to the inference that no large part of the suspended material settled at a rate between 1 cm. and 130 cm. in 4 months. The part of the suspension settling less than 1 cm. left the concentration of even the top fraction constant within the limits of experimental error; the particles settling more than 130 cm. were removed with the sludge. The application of Stokes' law to these two levels establishes two corresponding radii limits for each suspension between which there were no particles (Table 13). In other words, if the suspensions contained particles only larger and smaller than these limits, the observations made were in complete accord with the simple form of the kinetic theory. In four months the larger material could all deposit in the sludge, the

TABLE 13.—RANGE OF PARTICLE SIZE WHICH IF ABSENT IN SUSPENSIONS OF BURTON AND BISHOP WOULD MAKE THEIR OBSERVATIONS AGREE WITH CLASSICAL THEORY.

Gamboge	As_2S_3	Cu	CuO	Ag
46–525 mμ	13–153 mμ	8–86 mμ	9–105 mμ	7–78 mμ

smaller or "permanently" suspended material could not appreciably settle out in four months. Inasmuch as variations of 7° C. probably could not take place without somewhat disturbing the sedimentation, the upper limit for the "stable" material could well be greater than the lower limit given in the table.

As a matter of fact, several of these suspensions could well be relatively free of particles within the size limits suggested. It has been shown that a large part of the dispersed phase in metal sols by electro-pulverization or in appropriately prepared As_2S_3 sols is beyond the range of the ultramicroscope. In Table 14 are various values determined by Börjeson.[23]

TABLE 14.—PARTICLE SIZE IN THE FINE-GRAINED FRACTION OF VARIOUS SOLS.

Metal sols by electro-pulverization, arsenic trisulfide sol by precipitation.

Gold in water, ether, acetone and ethanol	r = ca. 3– 8 mμ
Silver in water and ethanol	" 5– 7 "
Cadmium in ether, acetone, ethanol and butanol	" 5–12 "
Copper in ethanol	" 7 "
Mercury in ethanol	" 20–30 "
As_2S_3 in water	" 11–16 "

Various electrical circuits [24] modify the ratio of coarse to fine particles, but do not greatly change the size of the small particles.

Freundlich and Kroch [25] conclude from X-ray analysis that the particles in Bredig copper sol are entirely oxide. By ultramicroscopic counting, they estimate the size of the finely divided material to be 18 mμ. Since a large part of the dispersed phase certainly could not be resolved in the ultramicroscope, and another fraction could be removed in the centrifuge, this "average" value of the size is undoubtedly considerably greater than for the slowest settling fraction remaining after centrifuging.[26] Sedimentation of arsenic trisulfide sols with small particles has also been described by Dumanski.[27] Using a vertical tube similar to Burton's, he observed a uniform rate of fall for over four years. The size of particle calculated by Stokes' law was 26 mμ, a reasonable value for such a sol. The constancy of the rate of fall over such a long period suggests a normal sedimentation rather than a coagulation process.

It therefore seems probable that the particle size in the metal and arsenic trisulfide sols was much less than Burton and Currie suspected. In the absence of definite data on the degree of dispersion of the suspensions, there is a certain probability that the experiments

[23] G. Börjeson, Diss. Upsala, 1921.
[24] E. O. Kraemer and T. Svedberg, *J. Am. Chem. Soc.*, 46, 1980 (1924).
[25] H. Freundlich and H. Kroch, *Z. physik. Chem.*, 124, 155 (1926).
[26] It is likely that a similar error in determining the size of particle in Bredig silver sol by ultramicroscopic counts gave rise to the surprising claim by Burton and Bishop that silver particles 170 mμ in radius do not settle under the influence of gravity.
[27] A. Dumanski, *Kolloid Z.*, 36, 98 (1925).

were entirely normal or ideal, in which case they give no information concerning the limits of validity of the simple form of kinetic theory. According to Mason and Weaver's analysis,[28] about 42 years would be required for the attainment of sedimentation equilibrium if Burton's suspensions contained particles of a size given by the lower limits of Table 13.

The same arguments are not so easily applied to the gamboge sols if, as seems likely, they were unfractionated suspensions. Gamboge suspensions normally contain particles covering a wide range of sizes, including the range given in Table 13. Near the upper limit (> 150 mμ) Perrin [29] has satisfactorily confirmed Stokes' law for the macrosedimentation of gamboge particles. Therefore after four months' undisturbed sedimentation in a Burton tube, there is every reason to expect that a normal gamboge suspension should show an increasing concentration with depth—not because of a sedimentation equilibrium, but because of a partial separation of different size classes during the course of settling. A uniform final concentration with a polydisperse gamboge suspension would constitute rather certain evidence that the sedimentation was disturbed externally.

On account of these several uncertainties, the writer prefers to consider the experiments of Burton and his co-workers as inconclusive for defining the limitations to the classical theory of colloidal suspensions. Although internal forces of some sort may have been operating which would place real limits to the ideal laws, it seems probable that they were more or less masked by spurious effects, some of which may be peculiar to experiments upon macrosedimentation. The elimination of spurious effects may be considered incomplete until all aspects of molecular-kinetic behaviour—Brownian motion, sedimentation equilibrium, fluctuations, diffusion, etc.—can be interpreted in terms of a single self-consistent theory. As yet, Burton has not availed himself of these various phenomena to furnish data supporting his modification of the kinetic theory for colloidal suspensions.

The other group of recent investigations of sedimentation which are inconsistent with the earlier studies have been carried out in the laboratories of Professor Porter.[30] Suspensions of gamboge, copper, silver and paraffin oil were allowed to sediment in a small glass cell (about $4 \times 4 \times 12$ mm.) within which ultramicroscopic counts of the relative number of particles could be made at various levels. Data of the distributions were published for fractionally centrifuged suspensions of gamboge (Fig. 7) and copper (Fig. 8), and polydisperse suspensions of silver (Fig. 8) and paraffin oil. They are summarized in Table 15. In all cases, the authors confirmed Burton's results by find-

[28] M. Mason and W. Weaver, *Phys. Rev.*, 23, 412 (1924).
[29] J. Perrin, "Die Atome." p. 90.
[30] A. W. Porter and J. J. Hedges, *Trans. Faraday Soc.*, 18, 91 (1922); 19, 1 (1923); W. W. Barkas, *ibid.*, 21, 66 (1925).

ing a region of practically uniform concentration at depths exceeding one millimeter. The curves show how markedly the observed distributions departed from the ideal behaviour indicated by the straight lines drawn through the authors' extrapolated values of log *n* for the surface level. The conclusion was reached that the ideal laws for sedimenta-

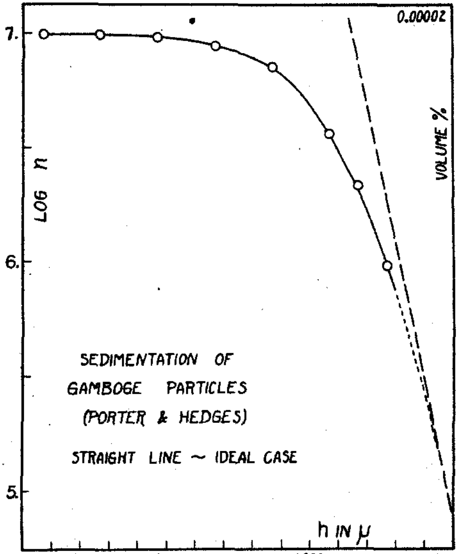


Fig. 7.

tion are valid only in an extremely thin layer near the highest surface of a suspension.

Porter and his co-workers, however, were not satisfied with Burton's electrical repulsion explanation of the observations, particularly because such forces should operate in all directions to produce non-uniform concentrations at side and bottom surfaces as well as the top. Instead, Porter and Hedges chose to adopt a van der Waals equation of state, as had previously been done by Svedberg, Perrin, and Costantin, with the simplification that the so-called internal pressure term *a*

was dropped, retaining only a "co-volume" term b to define the non-ideality of the suspensions as molecular-kinetic systems, i.e. $p=\frac{nRT}{N(1\text{-}bn)}$. This, it may be recalled, is in effect what Costantin had done by combining the a and b terms. The corresponding equation describing the theoretical sedimentation equilibrium (in accordance with the classical manner of derivation) becomes

$$\ln\frac{n}{1\text{-}bn}+\frac{1}{1\text{-}bn}=\frac{-Nvdgh}{RT}h+A$$

where A is a constant of integration theoretically determined by the

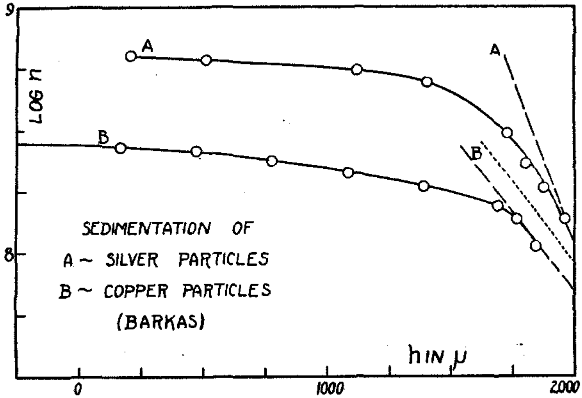


Fig. 8.

value of n_0 at the level $h=0$. The values of v, the "true volume"; n_∞, the uniform concentration at great depths; b, the collisional volume $(=1/n_\infty)$; and A were determined by empirically fitting the equation to the observed values of h and n, adjusting still further when necessary by means of a fourth arbitrary constant "correcting" h. These values are also shown in Table 15 as well as values for the depth range studied, the depth at which the concentration became equal to 0.9 n_∞, and the ratios of collisional volume to "true volume" b/v. The test of the theory that the uniform concentration in the body of the suspension is due to co-volume effects is seen to involve an equation with three or four arbitrary constants and unsatisfactory determinations of v.

TABLE 15.—SUMMARY OF SEDIMENTATION EXPERIMENTS BY PORTER AND HEDGES AND BARKAS.[1]

Authors	Particle	Radius[2] mμ	Depth Range, mm.	n_∞	Per Cent by Volume	Max./Min. Conc.	h for $0.9 n_\infty$, mm.	b	b/v
Porter and Hedges....	Gamboge	160	.23–1.43	10^7	.00002	10.3	.85	10^{-7}	6×10^8
	Paraffin Oil	2000	1.82–2.91+	10^8	.0034	2.7	?	10^{-8}	3×10^4
Barkas	Gamboge	145–170	?	3×10^9	.0045	?	?	3×10^{-10}	2×10^4
	"	170–300	?	2×10^8	.001	?	?	6×10^{-9}	10^8
	Paraffin Oil	175–200	?	$1–7 \times 10^8$	.0012	?	?	2×10^{-9}	10^8
	Copper	31–38	.152–3.0	3×10^9	.000006	2.7	3.5	3×10^{-9}	2×10^7
	"	43–50	?	10^8	.000004	?	?	10^{-9}	2×10^7
	Silver	?–44	.036–1.79	7×10^8	.00002	4.7	1.8	10^{-8}	5×10^8
	"	24–31	?	3×10^7	.0000003	?	?	4×10^{-9}	4×10^8

[1] All experiments were performed at "room" temperature. The time for equilibrium was not given.

[2] The radii, which are rough approximations, were determined either by fractional centrifuging in accordance with the theory of E. Talbot Paris, or from v upon the assumption that the Porter and Hedges theory and equation for the sedimentation equilibrium are correct.

These results present a number of points of unusual interest: the very large values of b; the surprisingly low values of n_∞ as a limiting concentration; the tremendous differences between corresponding b's and v's; the very low values of h at which the concentration became essentially uniform; and the influence which concentration is said to have upon these quantities.

The exact significance of such a large collisional volume remains unspecified. In terms of repulsive forces, the large b's require forces arising from the colloid particle to be highly effective through shells of water thousands of molecules thick. Very curious—and explained—is the apparently equal increase of the collisional volume with increasing dilution of the suspensions when different preparations are compared, although no corresponding increase need be assumed in levels of different dilution in a single preparation. Since in what appear to be duplicate experiments, the values of b may vary several hundred per cent, no relationships perhaps should be expected to be evident between b and density, size or kind of particle.

The "true volume" v behaved in an equally surprising manner. In different preparations of the same material, but of unequal concentrations, the volume of the solid particle as well as n_∞ appeared to be doubled when the concentration was doubled. On the other hand, v was not assumed to vary in levels of unequal concentration in a single preparation. This suggestion of changing v with changing dilution—when the dilution is brought about in a special way—has little if anything to recommend it; in fact, its acceptance demands the rejection of the authors' method of preparing monodisperse suspensions by fractional centrifuging which depends upon the invariability of the volume of a particle.

The uniformity of concentration in the main body of the suspension is equivalent to a zero "osmotic compressibility" $\left(\beta = -\frac{1}{n^2vdg}\frac{dn}{dh}\right)$. Such a system corresponds kinetically to an incompressible liquid, and might therefore be expected to require a more complicated equation of state than van der Waals, the absence of spontaneous fluctuations, and a modified Brownian motion. In reality, the spontaneous fluctuations were not absent, although their character was not compared quantitatively with theoretical expectations as Costantin did.

In addition to these points of interest, it is desirable to compare specifically the recent with the older conclusions concerning the validity of the ideal kinetic theory of suspensions. For a satisfactory comparison, it is unfortunate that the recent investigators have neglected to follow the precedent of their predecessors in the field in giving detailed information concerning the experiments. Thus, in the work under discussion, there are lacking the temperature, the time allowed for the attainment of equilibrium, and information with respect to the tests

for equilibrium. Inadequate attention was given to the rate of attainment of equilibrium conditions; only the statement appears that observations of concentration on a sample could not be made for more than two hours because of the disturbance of the distribution conditions. In no case were satisfactory determinations made of the particle size. The values given in the tables were obtained either from v, the "true volume," assuming the correctness of the authors' sedimentation theory, or from batch centrifuging, which is inherently incapable of giving precise results. For most of the experiments, the observed values of h and n were not published; from the manner in which they are summarized, it is impossible to reconstruct the original data. It is finally to be regretted that the transition from the non-ideal into the ideal distribution was not demonstrated.

In spite of these lacunæ in the data, it is certain that the results do not confirm the older conclusions that a high degree of ideality exists in the molecular-kinetic behaviour of dilute suspensions. The discrepancies appear in connection with the maximum concentration at which the behaviour is essentially ideal, the possible values for the collisional volume, and the actual distributions within a millimeter of the top surface.

With respect to concentrations in terms of particles per cc., Porter and his co-workers report in every case pronounced departure from ideal behaviour in concentrations exceeding 10^8 particles per cc. (in some cases as low as 10^6 particles per cc.) In contrast, the earlier work already surveyed in this examination failed to reveal any evidence of non-ideality in concentrations as high as 10^{15} particles per cc. by diffusion; 72×10^9 particles per cc. by spontaneous fluctuations; or 45×10^9 particles per cc. by sedimentation equilibrium. With respect to volume concentrations, the recent investigators report a marked non-ideality in gamboge or oil suspensions as dilute as 0.001 per cent—or even 0.00001 per cent; and in heavy metal suspensions as dilute as 0.00001 per cent—or even 0.0000003 per cent. In contrast, the earlier investigators found ideal behaviour in corresponding systems in concentrations as high as 0.0018 per cent by diffusion; 0.023 per cent—or even 0.75 per cent by spontaneous fluctuations; and 0.003 per cent—or even 0.75 per cent by sedimentation equilibrium.

A comparison of recent and earlier work may also be made in terms of b/v ratios. The *minimum* values inferred for different samples in the recent work varied between 2×10^4 and 4×10^8—most of the values being ca 10^7. In contrast, the earlier work, to the extent that it demonstrated ideal behaviour, gives b/v as equaling 1, with the exception of Costantin's value of 20 obtained from sedimentation equilibrium and fluctuations. Instead of taking the value 1, it is more accurate to compare the maximum possible values which b/v could have without causing a departure from ideality exceeding 10 per cent (the

probable uncertainty in Westgren's work apparently is not so great). The relative change in the osmotic compressibility of a system due to the co-volume effect is proportional to $(1-bn)^2$; in the ideal case, $b = 0$ and the factor equals 1. The maximum experimental error of 10 per cent may be applied to this factor, and the maximum values of b calculated for various investigations. Westgren's most favorable experiment on fluctuations shows that b/v is less than 225; the most favorable example of sedimentation equilibrium gives 1600 as a maximum; and his most favorable case of diffusion shows that b/v could not exceed 2900. How much less the b/v values actually were, the experiments do not show, for the non-ideality was not sufficient in any case to allow precise measurement of its degree.

Finally, the two groups of data are inconsistent with respect to the depth range within which ideal conditions existed. Using gamboge particles, Perrin and Costantin found ideal behaviour over depths of 0.015-0.100 mm., depending upon the equilibrium concentration at the surface. Westgren's results with small heavy metal particles comparable to those used by Barkas found ideal behaviour over a range of several tenths to 1.1 mm. when the surface concentration was approximately 10^9 particles per cc. Inasmuch as the recent investigators report but one observation at a level less than 0.1 mm. from the surface, no positive information is available concerning the ideality or non-ideality near the surface in their experiments. If their empirical values of A, b and v and their extrapolation of the distribution curve into the surface layers be accepted, the ideal and extrapolated values of n at say 0.1 mm. depth may be calculated and compared.[31] It is thus found that the ideal concentration at the 100 μ level in Porter and Hedges' gamboge experiment is only 3 per cent higher than the extrapolated. Barkas' data, however, on copper and silver suspensions show a discrepancy of 19 and 31 per cent respectively at the 100 μ level. In other words, if the Porter and Hedges formulation of sedimentation is correct, the "Perrin layer"—showing an approximately ideal behaviour—must have been vanishing thin, and certainly not more than one-twentieth the maximum range in which Westgren reported ideal distribution.

These comparisons can leave no doubt of the contradictions in the facts reported. It is however not so easy to locate their source. To one impressed by the successes of the simple form of the kinetic theory applied to suspensions, and cognizant of the manipulative difficulties and snags in this field, there is a persuasive temptation to suspect that insufficient precautions against sources of error may have been taken in the recent investigations; this suspicion is encouraged by the absence of relevant and significant data as has already been pointed out.

[31] *If b increases with dilution as Porter and Hedges suggest, the actual discrepancies must be even greater than here indicated.*

Certain of the possible sources of error were recognized and specifically mentioned. Thus Barkas states that "the greatest difficulty was experienced in the liability to convection currents in the solution, and their causes were never entirely eliminated . . . it was seldom possible to work for more than 2 hours consecutively . . . owing to drifting of the particles." He also notes that changes in the illumination rendered many sets of counts obviously false even in the course of a satisfactory experiment and had to be rejected before averaging. Because of the greater size of the cell containing the suspensions, it is quite possible that drifting and convection were more pronounced than in the thin cells used by earlier investigators. In view of the rapidity with which drifting became noticeable, it is not easy to be confident that ideal equilibrium conditions were ever attained.

Even if drifting did not occur during the sedimentation, it seems possible that insufficient time was given to attain equilibrium. According to the analysis of Mason and Weaver [32] the time required for approximate attainment of equilibrium in an ideal system lies between once and twice the time necessary for a single particle to fall the length of the column. In Barkas' experiments, the column was approximately 1.2 cm. high. Values of twice the time of fall and of the characteristic constant alpha for particles approximating those of Barkas' in size follow.

TABLE 16.—TIME FOR ATTAINMENT OF SEDIMENTATION EQUILIBRIUM ACCORDING TO CRITERION OF MASON AND WEAVER.

	Radius	2 × Time of Fall	α
Gamboge	150 mμ	680 hours	0.012
Copper	40 "	240 "	.016
Silver	30 "	360 "	.031

The authors make no mention of any such periods of quiet sedimentation. Furthermore, as comparison with Figure 1 of Mason and Weaver's shows, the distribution curves observed by Porter, Hedges and Barkas closely resemble the upper portion of the curves representing the transient conditions theoretically existing in such systems after a few hours of sedimentation. In both cases, there is an inflection point near the surface and a uniform concentration in the body of the suspension. In the theoretical case, the uniform concentration increases rapidly very near the bottom. Unfortunately, the bottom of the cell apparently was not examined by the English workers.

These considerations lead to the conclusion that the questions concerning the limits of validity of the ideal kinetic equations as a description of the behaviour of colloidal suspensions remain unanswered by the recent studies of sedimentation. The problem of stability of such

[32] *Loc. cit.*; also W. Weaver, *Phys. Rev.*, 27, 499 (1926).

suspensions has the same status. It has not yet been proven that the forces which prevent collision and adherence of the particles also give rise to the more or less uniform concentration commonly observed in these systems, even when dilute. If these stabilizing forces were to operate with such long ranges as to prevent sedimentation under the influence of gravity, there is every reason to believe that the same forces would likewise reveal themselves in such phenomena as Brownian motion, diffusion, spontanous fluctuations, as well as sedimentation. Until these various phenomena yield the same conclusions concerning the non-ideality in the kinetic behaviour of suspensions, isolated cases of discrepancy between observations and theory may be suspected to be due to spurious effects of an external character.

University of Wisconsin,
Madison, Wisconsin.

THE MEASUREMENT OF ADHESION TENSION SOLID AGAINST LIQUID

By F. E. Bartell and H. J. Osterhof

There is no controversy over the statement that glass is wetted by water; there does, however, appear to be a difference of opinion as to the correctness of the statement that glass is wetted by mercury. Further thought along this line will make it evident that the commonly used terms, such as "wet," "wettability," "wetting power," etc., are general terms which, up to the present time, have been but poorly defined.

Consider that one has two different solid substances completely in contact with, or entirely covered by a liquid. In what terms or units shall we compare the relative wettability of the solids or further, in what terms shall we compare the "wetting power" of different liquids for a given solid?

We shall accept the view that *various solids* are wetted to different degrees by a given liquid; also that a *given solid* may be wetted to different degrees by various liquids. We believe further that the wetting power of each of the various liquids is specific in relation to a given solid. Unfortunately, there are no tables available in the literature which will give even the *relative* wettability of a solid by different liquids.

Various methods have been suggested for measuring the wetting power of liquids and among these has been the determination of the surface tension of the liquids in question.[1] Vermorel and Dantony at first believed that surface tension values, as determined by the capillary tube method, gave a satisfactory indication of the wetting power of a liquid, but they later[2] decided that surface tension data alone was not sufficient to determine the wetting power.

It is now quite generally appreciated that "wetting power" is a function not only of the surface tension of a liquid, but also of the *specific* attractions operative between the solid and liquid. An indication of the magnitude of this attraction or force of adhesion solid-liquid[3] can be obtained in case the contact angle solid-liquid is known.

Degree of Wetting.—Throughout this paper we shall use the following symbols:

[1] Brunnich and Smith, *Queensland Agri. J.*, 2, 81 (1914); Vermorel and Dantony, *Compt. rend.*, 151, 1144 (1911).
[2] *Compt. rend.*, 154, 1300 (1912).
[3] The expression solid-liquid is used to indicate solid in contact with liquid and similar expressions are to be taken as having a similar meaning.

S = surface tension, interfacial tension, (or free surface energy)
A = adhesion tension
θ = Contact angle
Wa = work of adhesion
Subscripts 1, 2 and 3 will represent solid, organic liquid and water phases, respectively.

It has been definitely shown that water forms a zero angle of contact with glass.[4]

In those cases in which there exists a zero contact angle between solid and liquid, the solid will tend to become wetted spontaneously and completely by the liquid in contact with it. It follows from the well known principles of capillarity that the surface tension of the solid-air system must then be greater than the sum of the surface tension of the liquid and the interfacial tension of the solid-liquid system; i.e.,

$$S_1 > S_2 + S_{12}.$$

At the other extreme it is likewise perfectly evident that no wetting of solid by liquid will occur in case the contact angle is 180°. Surfaces of such materials will come together with no decrease of free surface energy, i.e.,

$$S_1 + S_2 = S_{12}.$$ [5]

In those cases in which contact of liquid with solid results in a decrease of free surface energy, there must be the following relationship:

$$S_1 + S_2 > S_{12} \quad \text{or} \quad S_1 + S_2 = S_{12} + \Delta F,$$

where ΔF represents the decrease in free surface energy. The contact angle, therefore, must be less than 180°. It is obvious that in such cases, adhesion will occur, since ΔF or the work of adhesion is positive. Strictly speaking, then, the solid will become wetted by the liquid. Mercury and glass give a contact angle of about 130°.[6] Since this is less than 180° mercury will, in reality, wet glass.

When the solid-liquid contact angle is equal to 90°, the force of adhesion may be shown to be equal to one-half the force of cohesion of the liquid molecules for each other. When the contact angle is between 90° and 180°, the force of adhesion solid-liquid is less than one-half the force of cohesion liquid-liquid and a drop of liquid placed on a solid will pull itself together and recede from the solid until its characteristic contact angle is reached. Nevertheless, wetting, according to our views, actually does occur to a certain definite extent. If the solid be forcibly inserted into the liquid we may say that the solid

[4] Richards and Carver, *J. Am. Chem. Soc.*, 37, 1643 (1915).
[5] S_1, S_2 and S_{12} may be considered as representing the free surface energy of the systems in question.
[6] Furth, *Sitz. Akad. Wiss-Wien.*, 126, 329 (1917).

is now wetted by the liquid to a certain definite degree, the degree being dependent upon the magnitude of the decrease in free surface energy.

When the solid-liquid contact angle is between 0° and 90°, the force of adhesion solid-liquid is greater than one-half the force of cohesion liquid-liquid, and such a liquid when placed on the solid will tend to spread upon its surface. In all such cases the extent of spreading

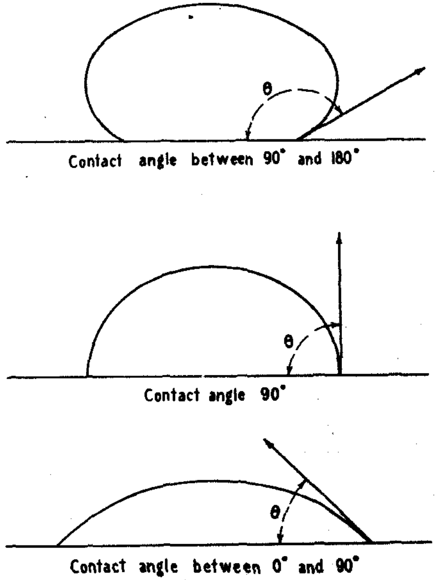


FIG. 1.

will be limited by the surface tension of the liquid and by the contact angle which is characteristic of this system. In the case of a solid-liquid system which gives a zero contact angle the force of adhesion must then be equal to, or greater than the force of cohesion liquid-liquid.

Adhesion Tension.—We believe that the degree of wetting of a solid by a given liquid can best be expressed in terms of the *adhesion tension* solid-liquid. We shall first define adhesion tension and later shall describe the method which we have developed for its measure-

ment. By the use of this method it is possible to determine experimentally the values of adhesion tension in terms of the absolute units. Thus we may say that it is in fact possible to refer to the degree of wetting of a solid by a given liquid in terms of absolute units.

Thomas Young[7] in 1805 derived an expression for the equilibrium conditions existing in a solid-liquid system in terms of the contact angle and the different interfacial tensions. This expression is

$$S_1 - S_{12} = S_2 \cos \theta \qquad (1)$$

In words, the difference between the interfacial tensions solid-air and solid-liquid is equal to the surface tension liquid-air times the cosine of the angle of contact. This equation has also been developed by Poincare in his treatise on Capillarity, and by Dupré in "La Théorie Mechanique de la Chaleur." It was formulated and employed by Quincke,[8] and also by various investigators up to the present. This equation, though well known and entirely sound from the standpoint both of mechanics and thermodynamics, has not received the consideration that it appears to deserve.

Freundlich[9] has stated that "adhesion tension" is equal to a fractional part, given by the cosine of the angle of contact, of the surface tension of a liquid; i.e.,

$$A_{12} = S_2 \cos \theta \qquad (2)$$

Then, from equation (1),

$$A_{12} = S_1 - S_{12} \qquad (3)$$

The adhesion tension is thus the numerical difference in dynes per cm. or ergs per sq. cm. between the surface tension of the solid against air and its interfacial tension against the liquid. It may be defined as the decrease in free surface energy which occurs when a unit interface solid-liquid is substituted for unit interface solid-air. It is accordingly the energy factor upon whose magnitude depends the wetting or non-wetting of a liquid for a solid surface.

It is obvious that the greater the attraction solid-liquid the smaller must be the interfacial tension, and the smaller the interfacial tension, S_{12}, the greater will be the adhesion tension solid-liquid. It is therefore apparent that adhesion tension is in reality a measure of the attraction of a liquid for a solid, likewise of its "wetting power" for that solid.

In a great many cases we find that the degree of wetting of a solid by a liquid is so high that the contact angle is zero. This means that not only is the force of adhesion solid-liquid sufficient to bring the contact angle down to a zero value, but it may in fact be much greater

[7] *Phil. Trans.*, p. 65 (1805).
[8] *Wied. Ann.* (N. F.) 2, 145 (1877).
[9] "Colloid Chemistry," E. P. Dutton & Co., New York, 1926, p. 157.

than is represented by this, with the result that the equation is indeterminate. A general and more fitting expression then is

$$A_{12} = S_1 - S_{12} = K\,S_2 \qquad (4)$$

where K may be called the adhesion constant. We shall see later that by the use of our method of measurement the value of K, which may be greater than unity, as well as adhesion tension, can be determined, even though the actual contact angle is zero.

General Method Employed.—It is obvious from the above that the adhesion tension solid-liquid may be determined provided we can obtain values for the surface tension of the lqiuid in question and for the contact angle solid-liquid.

The value for the surface tension of a liquid is readily obtained by any of the well known methods. A large amount of such data is available in the literature. Reliable values for contact angles are on the other hand exceedingly scarce; in fact, one might say that they are practically non-existent in the literature.

It has often been pointed out that in addition to direct optical measurement, contact angles can be measured by determining the surface tension of a liquid by two different methods. One of these methods should give the value of surface tension independently of the contact angle, as in the falling drop or escaping bubble method; and the second method should be dependent on an equation involving both surface tension and contact angle, as with the capillary tube method. It is rather surprising that no one has heretofore followed up this procedure with much success.

The method herein described does in effect make use of this principle, the capillary tube method being used in both instances. In one case a liquid which is known to give a zero contact angle with the (solid) walls of the tube must be used within the capillary. This enables us to establish the necessary characteristics of the tube (i.e., tube radius, displacement pressure, etc.). Next is used a liquid which does give a definite contact angle with the walls of the tube. The value of this angle can then be calculated by use of the well known formulation:

$$\cos\theta = \frac{rhdg}{2\,S} \qquad (5)$$

Development of Method and Apparatus.—Certain features attendant on the actual development of our method are of interest. Early in our work on the relative wettability of solids by liquids we attempted to carry out different modifications of the methods used by Hofmann,[10] Reinders[11] and others who added a powdered solid to a vessel containing two immiscible liquids, as water and an organic liquid.

[10] *Z. physik. Chem.*, **83**, 385 (1913).
[11] *Kolloid Z.*, **13**, 235 (1913).

The solid powder will go either to the water (Liq. No. 3), to the organic liquid (Liq. No. 2), or will remain at the interface between these two liquids, its position depending upon the relative interfacial tension values of the system. These well-known relationships follow:

a — If $S_{12} > S_{13} + S_{23}$	the solid will go completely to Liquid No. 3
b — If $S_{13} > S_{12} + S_{23}$	" " " " " " " " 2
c — If $S_{23} > S_{12} - S_{13}$	" " " " " " " Interface.

In case no interfacial tension is greater than the sum of the other two, the solid will remain at the interface, but will in all but exceptional cases be wetted more by one liquid than by the other.

The system may be said to be in equilibrium when

$$S_{12} = S_{13} + S_{23} \cos \theta \tag{6}$$

If $S_{12} > S_{13}$, cos θ must be positive and the contact angle is therefore less than 90°. Under these conditions (and disregarding effects due to gravity) the greater part of the solid will be in Liquid No. 3; i.e., assuming the particle to be spherical, its equator will be in Liquid No. 3. Theoretically it would be possible to measure this contact angle. Practically this method has as yet offered no satisfactory means for the determination of the contact angle or of absolute values of adhesion tensions or pressures.

A qualitative indication of the relative wetabilities can be obtained by noting the tendency of solid particles to distribute themselves between such liquid phases. Hofmann, Reinders, and others have given "relative "wetting" tables based upon such qualitative methods.

Work similar to the above finally led us to try the plan of compressing powdered solid material, forming thereby a type of membrane with capillary pores between the particles.

An immiscible liquid-liquid interface was formed within these capillaries (i.e., part of the compressed powder was wetted by one liquid, the remainder by the other). It was found that with the solid particles thus fixed, the liquid interface would move. If prevented from moving by an applied opposing pressure, a definite pressure would be necessary to prevent such movement, that is, to prevent the displacement of one liquid from the pores of the solid material, by the other liquid.

Apparatus.—After several attempts a simple form of apparatus was used with which could be followed the rate of displacement of water from carbon black by organic liquids, and of organic liquids from silica by water. Although the measurement of the rate of displacement gave consistent and comparable values, this measurement was discontinued after additional improvements in apparatus were made and

instead the *pressure of displacement* of one liquid by another was measured. Full description of the apparatus which is now employed and the detailed method of its application will soon appear in another paper from this laboratory. A brief description, however, will be given here. The displacement cell consists essentially of a brass cylindrical tube, open at both ends, with closely fitting perforated plungers which can be inserted in these ends. The cell is of such a size that the membrane contained in it at the end of the packing process forms a cylinder approximately three inches long by one inch in diameter. At the outer extremity of each of the plungers is sealed a glass capillary tube, one tube serving as a displacement indicator, the other by means of a ground glass joint furnishing connection with a manometer. Powdered solid of uniform size thoroughly wetted by the liquid to be displaced (or by air) is packed in the manometer end of the cylindrical tube by a hydraulic press under a pressure of 2500 pounds until the tube is about two-thirds filled. Against this is then packed some of the solid material wetted by the displacing liquid. While the cell is still in the press the plungers are secured in place by a steel yoke and bolts, keeping the pressure of packing constant at 2500 pounds. The joint between plunger and cylinder is then rendered leak-proof by screwing down a threaded nut and gasket. This apparatus when assembled has been tested up to thirty atmospheres pressure and found to be air tight.

After the displacement cell has been filled and assembled the pressure end is connected to the manometer and the equilibrium pressure measured. In a large number of determinations of liquid-liquid systems against carbon black and against silica, close agreements in duplicate experiments were almost invariably obtained. Over a range of pressures from 8 gms. per sq. cm. to 7000 gms. per sq. cm. with different liquid systems, duplicates usually checked within five-tenths of one percent.

Some typical data are given in Table 1 which show the magnitude and variation of the displacement pressures obtained in certain liquid-liquid systems. Organic liquids all displace water from carbon black, while with silica the direction of displacement is reversed. The difference in magnitude of the displacement pressures with silica and carbon is largely due to the fact that the carbon is much more finely divided.

Method for Measuring Adhesion Tension.—Strictly speaking, the method is limited firstly, to solids which can be finely ground and the particles of which can be firmly compressed so as to give uniform packing. The individual particles must possess such rigidity as to resist deformation sufficient to close the voids between the particles; in other words, the porosity of the compressed powder must be readily

TABLE 1.—DISPLACEMENT PRESSURES.

Temperature = 25°C.

Liquid	Surface Tension	Interfacial Tension with Water	Carbon[1] (Organic Liquid Displaces Water) Pressure in Gms. per Sq. Cm.	Silica[2] (Water Displaces Organic Liquid) Pressure in Gms. per Sq. Cm.
Benzene	28.25	34.65	5775	295
Toluene	27.70	36.10	6005	273
Hexane	17.82	50.25	3330	395
Carbon tetrachloride	26.12	44.54	6935	409
Carbon disulphide	32.30	46.30	7610	358
Butyl acetate	24.06	13.17	2420	91
Alpha-bromo naphthalene	44.00	42.07	7550	397

[1] With carbon, pore radius, $r_1 = 9.3 \times 10^{-6}$ cm.
[2] With silica, pore radius, $r_1 = 2.1 \times 10^{-4}$ cm.

reproducible. These pores must in effect serve as capillary tubes in our measurements. Secondly, liquids must be used which will—when taken in appropriate pairs—form immiscible binary liquid systems.

Data (unpublished) has been obtained which shows, from theoretical and experimental considerations, that when portions of a powdered solid are compressed under a uniform pressure, membranes are formed whose interstices are in effect capillary pores of approximately circular cross-section and of fairly constant radius. The effective radius of these pores can be closely duplicated in successive membranes, and can be measured with equal accuracy by methods based on Poiseuille's formulation or on the capillary rise formulation. Furthermore, we have shown that in the cases of several different solid surfaces the liquid-solid contact angle has a definite and reproducible value. Consequently any reactions occurring within the interstices of the compressed powdered solid may be accorded the same theoretical treatment which would be employed for similar reactions in a single uniform glass capillary tube.

As an illustration let us consider Figure 2(a) in which we may represent a liquid 2 (surface tension $= S_2$) in contact with solid (surface tension $= S_1$) in the presence of air. The interfacial tension solid-liquid $= S_{12}$ and we have

$$S_1 - S_{12} = S_2 \cos \theta_{12}$$

or

$$A_{12} = S_1 - S_{12} = S_2 \cos \theta_{12} \qquad (7)$$

In Figure 2(b) we have represented liquid 3 in contact with the solid and then we have

$$S_1 - S_{13} = S_3 \cos \theta_{13},$$

$$A_{13} = S_1 - S_{13} = S_3 \cos \theta_{13} \tag{8}$$

In Figure 2(c) we have liquids 2 and 3 in contact with solid and accordingly

$$S_{13} - S_{12} = S_{23} \cos \theta_{23} \tag{9}$$

Combining equations 7 and 8 we have

$$A_{12} - A_{13} = S_{13} - S_{12} \tag{10}$$

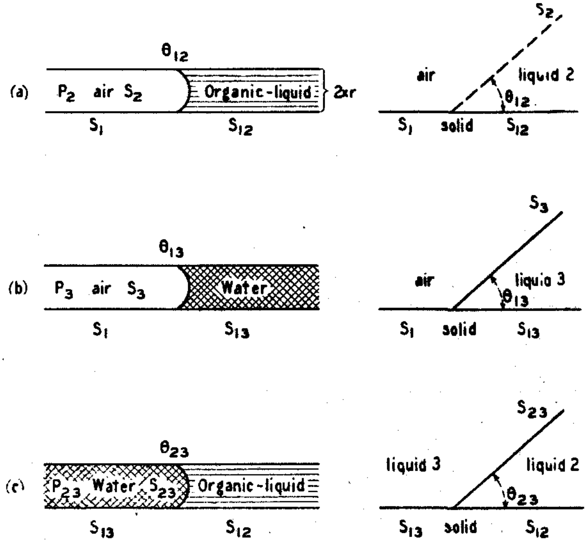


FIG. 2.

It then follows from equation 9 that

$$A_{12} - A_{13} = S_{23} \cos \theta_{23} \tag{11}$$

Suppose, for example, that we have a given solid and wish to determine the adhesion tension between that solid (let it be carbon) and a liquid 2 (let it be an organic liquid) and we find that the organic liquid gives

with the solid a zero contact angle. That leaves then no (previously known) method for this determination. We may, however, obtain this value by use of the method described herein. The solid to be used is ground to 300 mesh or finer. It is uniformly compressed in the displacement cell under a definite pressure of from 100 to 200 atmospheres. A manometer or pressure gauge is affixed to one end of the cell.

A liquid (assume that it is benzene) which is known to give a zero contact angle with the solid (carbon) is brought in contact with the compressed solid particles within the cell. Air is displaced toward the manometer side. Air pressure is increased on that side so as to prevent actual movement of liquid within the capillary spaces of the material. Readings are noted on the manometer. In time we find that no additional pressure is necessary in order to prevent further movement of the liquid column. This is taken as the equilibrium pressure.

Since the liquid gives no contact angle with the pore wall and since the pore is so small that second order corrections are unnecessary, the following simple capillary formulation applies:

$$S_2 = \frac{rhdg}{2} \tag{12}$$

Substituting P_2 for hd and transposing

$$r = \frac{2S_2}{P_2 \times 981} \tag{13}$$

The pore radius r may then be calculated by inserting the observed value for P_2 (displacement pressure of liquid 2) and S_2 the surface tension of the liquid.

We shall next use a liquid (assume it to be water) which we have reason to believe will give a definite contact angle with the solid. We proceed with measurements as above and determine the displacement pressure (P_3) of air by this liquid. By making use of the equation

$$\cos\theta_{13} = \frac{r \times P_3 \times 981}{2S_3}, \text{ (from Eq. 5)} \tag{14}$$

the value of $\cos\theta_{13}$ can be calculated, since r, P_3, and S_3 are known. It is obvious that when both $\cos\theta_{13}$ and S_3 are determined the adhesion tension of solid-liquid 3 can be obtained, since

$$A_{13} = (S_1 - S_{13}) = S_3 \cos\theta_{13}. \text{ (from Eq. 8)}$$

The next step is the determination of the adhesion tension of solid-liquid 2, or the adhesion tension between this same solid and any other liquid, which gives a zero contact angle with the solid. (For

this purpose the two liquids used must be brought together in contact with the solid, as in Figure 2 (c).) We must now measure the pressure with which liquid 2 will displace liquid 3. Accordingly, finely divided solid wetted with liquid 3 is compressed within the cylinder. Liquid 2 is brought in contact with liquid 3 which is within the pores of the solid and commences to displace the latter liquid. The displacement pressure is measured as before. We now make use of the equation

$$\cos \theta_{23} = \frac{r \times P_{23} \times 981}{2\,S_{23}} \quad . \tag{15}$$

In this way we determine what may be termed the interfacial solid-liquid 2- liquid 3 contact angle.

From this result the value of

$$S_{12} - S_{13}, \text{ or its equivalent } A_{13} - A_{12} \text{ (Eq. 11)}$$

can be determined. This then gives the difference between the adhesion tension values for the two different solid-liquid systems. Having previously obtained the value of A_{13} (the adhesion tension carbon-water) the value of A_{12} can be determined.

It is thus possible to determine the adhesion tension of a solid-liquid system even though the contact angle solid-liquid may be zero. The above relationships are all evident from a consideration of Figure 2. (The method of calculation may be readily understood by noting the data from an actual experiment).

There is now available all the data necessary for our calculations, since there are on hand the following values:

(1) Surface tension liquid $2 = S_2$
(2) Surface tension liquid $3 = S_3$
(3) Interfacial tension liquid 2-liquid $3 = S_{23}$
(4) Contact angle solid-liquid $3 = \theta_{13}$
(5) Interfacial contact angle solid-liquid 2-liquid $3 = \theta_{23}$

Example:

Consider the system carbon-benzene-water.
Benzene forms a zero contact angle with carbon.
Water forms a definite contact angle with carbon.
Benzene-water interface gives a definite contact angle with carbon.

1. Benzene displaces air from carbon with a pressure $P_2 = 6200$ gms./cm^2.

$$r = \frac{2\,S}{P_2 \times 981} = \frac{2 \times 28.25}{6200 \times 981} = 9.3 \times 10^{-6} \text{ cm.}$$

2. Water displaces air from carbon with pressure $P_3 = 12000$ gms./cm².

$$\cos \theta_{13} = \frac{r \times P_3 \times 981}{2\, S_3} = \frac{9.3 \times 10^{-6} \times 12000 \times 981}{2 \times 72.08} = 0.7595$$

$$\theta_{13} = 40° \; 35'$$

3. Benzene displaces water from carbon with pressure $P_{23} = 5775$ gms./cm²

$$\text{Then } \cos \theta_{23} = \frac{r \times P_{23} \times 981}{2\, S_{23}} = \frac{9.3 \times 10^{-6} \times 5775 \times 981}{2 \times 34.65} = 0.7603.$$

Since $A_{13} = \cos \theta_{13} S_3$

$A_{13} = 0.7595 \times 72.08 = 54.74$ dynes per cm.

= adhesion tension carbon-water,

and since

$A_{12} - A_{13} = \cos \theta_{23} S_{23}$

we have

$A_{12} - A_{13} = 0.7603 \times 34.65 = 26.34$ dynes per cm.

or $A_{12} = A_{13} + 26.34$.

$A_{12} = 54.74 + 26.34 = 81.08$ dynes per cm.

= adhesion tension carbon-benzene.

In Table 2 is given a short list of typical adhesion tensions expressed in dynes per cm. for several liquids against silica and against carbon black.

TABLE 2.—TYPICAL ADHESION TENSIONS FOR CERTAIN LIQUIDS AGAINST CARBON BLACK AND SILICA.

	Carbon Black		Silica	
Liquid	Pressure Gms. per Sq. Cm.	Adhesion Tension Dynes per Cm.	Pressure Gms. per Sq. Cm.	Adhesion Tension Dynes per Cm.
Water	...	54.74	...	82.82
Benzene	5775	81.08	295	52.43
Toluene	6005	82.13	273	54.70
Hexane	3330	69.93	395	42.13
Carbon tetrachloride	6935	86.37	409	40.69
Carbon disulfide	7610	89.45	358	45.94
Butyl acetate	2420	65.78	91	73.45
Alpha-bromo naphthalene	7550	89.18	397	41.92

These values were calculated in the manner just shown. In the case of silica the pressure is caused by the displacement of the organic liquids by water. In the case of carbon the pressure is caused by the displacement of water by the organic liquid.

Free Surface Energy Changes and Work of Adhesion.—Consideration of the principle of virtual work shows that it is proper to substitute for a uniform free surface energy a uniform surface tension. Accordingly it is justifiable to use the values for surface tensions to simplify the theoretical treatment of those phenomena which occur in solid-liquid systems because of the free surface energy changes. The tensions must be considered as constant and acting tangentially to the surface.

Let us consider the free surface energy relationships of a solid-liquid system.

Let S_1 = free energy per unit area of solid,
S_2 = free energy of unit liquid surface, and
S_{12} = free energy of their interface.

To obtain a more definite concept of adhesion tension solid-liquid it may well be compared with the expressions for interfacial tension and work of adhesion. The energy changes that occur as a result of the contact of the two phases are summed up by the familiar expression

$$Wa_{12} = S_1 + S_2 - S_{12}. \quad (16)$$

This may also be expressed as

$$Wa_{12} = (S_1 - S_1') + (S_2 - S_2'). \quad (17)$$

S_1 and S_2 are to be considered as representing the energy available, owing to the existence in a state of strain of the free surfaces of the solid and of the liquid, and are measured in ergs per square centimeter. S_1' and S_2' then represent the decreased free surface energy possessed by the two surfaces after the formation of the interface, the decrease being occasioned by the partial relief of the strain. The sum of these two latter values is the interfacial tension, or

$$S_{12} = S_1' + S_2'. \quad (18)$$

This represents the energy due to unsatisfied forces still resident in the interfacial layer. Moreover, since

$$A_{12} = S_1 - S_{12} = KS_2 = S_2 \cos\theta \text{ (when } \theta > 0) \quad (19)$$

the work of adhesion is also given by the expression

$$Wa_{12} = A_{12} + S_2. \quad (20)$$

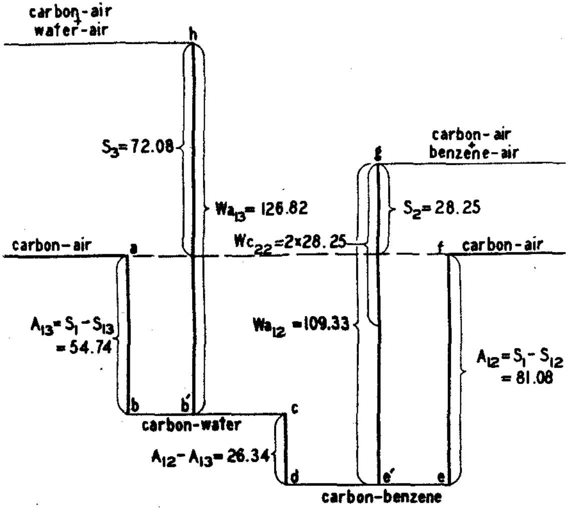
That is, the work of adhesion is equal to the adhesion tension solid-liquid plus the surface tension of the liquid, or in terms of the contact angle:

$$Wa_{12} = \cos\theta_{12} S_2 + S_2 \text{ (or } KS_2 + S_2) \quad (21)$$

or

$$Wa_{12} = (K + 1)\, S_2 . \tag{22}$$

It may be seen from the above equations that the evaluation of A_{12} is possible if S_2, the surface tension, and the constant K can be determined. It may again be pointed out that in all previous work K and A_{12} have been determinable only when the contact angle is greater than zero.



ENERGY LEVELS CARBON AGAINST WATER AND AGAINST BENZENE

FIG. 3.

The relationship of adhesion tension and work of adhesion is readily understood from a study of the diagram shown in Figure 3. This diagram will illustrate the relationship between the various surface energy values which have been considered in our measurement of adhesion tension. Consider the determination of the work of adhesion carbon-water.

We shall start with the carbon-air interface. Its free surface energy value, S_1, is unknown and is with present methods undeterminable. Suppose we now bring the liquid, water, in contact with the carbon thus forming a carbon-water interface. A decrease in free surface energy will result. This decrease in free surface energy is equal to the work of adhesion. The work of adhesion, as has been shown, is numerically equal to the adhesion tension solid-liquid plus the surface tension of the liquid, S_3.

The adhesion tension is equal to the interfacial tension solid-air minus the interfacial tension solid-liquid; neither of these values is known; furthermore, there is as yet no method for determining them. However, we have shown it possible to determine the difference between them, which gives the adhesion tension, from the equation

$$A_{13} = S_1 - S_{13} = S_3 \cos \theta_{13} .$$

For carbon and water the value is

$$A_{13} = 72.08 \times \cos 40° \, 35' = 54.74 \text{ ergs per sq. cm.}$$

This furnishes an indirectly obtained value for $S_1 - S_{13}$ which, expressed in terms of energy units, is 54.74 ergs per sq. cm.; that is to say, the energy level at the interface has been reduced 54.74 ergs per sq. cm. below the energy level of the carbon-air interface; this is represented by line *ab*.

The total decrease in free surface energy is expressed by the equation

$$\Delta F_{13} = A_{13} + S_3,$$

or

$$\Delta F_{13} = 54.74 + 72.08 = 126.82 \text{ ergs per sq. cm.}$$

This decrease in free surface energy, in fact, represents the work of adhesion carbon-water. The work of adhesion, Wa_{13}, is represented by line *b'h*.

As previously pointed out, the work of adhesion of carbon-benzene cannot be determined by even this indirect method, for the reason that benzene and carbon give a zero angle of contact. This makes it impossible to obtain the adhesion tension value for carbon-benzene by such a treatment.

The connecting link in this determination is the fact that it is possible, through the simultaneous contact of benzene and water with carbon, to measure the interfacial angle formed and therefrom (equations 9 and 10) to calculate the difference between their adhesion tensions $A_{12} - A_{13}$. This value for the carbon-benzene-water system is equal to 26.34 dynes per cm., which shows that the carbon-benzene interface is at a lower energy level than the carbon-water to the extent of 26.34 ergs per sq. cm. This is represented by line *cd*.

It is for this reason that benzene will displace water from carbon, for by so doing the system can pass to a lower energy level.

We are now in a position to determine the adhesion tension A_{12} for carbon-benzene:

$$A_{12} = A_{13} + 26.94 = 54.74 + 26.34 = 81.08 \text{ ergs per sq. cm.},$$

the adhesion tension. This is represented by line *e f*. And further, since the work of adhesion of carbon and benzene is equal to the adhesion tension carbon-benzene plus the surface tension of benzene,

$$Wa_{12} = A_{12} + S_2\text{; i.e.,}$$
$$Wa_{12} = 81.08 + 28.25 = 109.33 \text{ ergs per sq. cm.}$$

or the work of adhesion between carbon and benzene is 109.33 ergs per sq. cm. This is represented by line *e′g*.

It is interesting to note that even though the adhesion tension of carbon with benzene is greater than that of carbon with water, the work of adhesion of carbon with benzene is less than the work of adhesion of carbon with water.

These data show clearly that a measure of the decrease in free surface energy of systems of a given solid with different liquids need not give reliable data as to the relative degree of wetting of the solid by the different liquids, as has heretofore been assumed by some investigators.

It is usually assumed that the work of cohesion of a liquid is equal to twice the value of its surface tension or $Wc = 2S$. It follows that the work of cohesion of benzene (for itself) is equal to 2×28.75 or 56.50 ergs per sq. cm. This is considerably less than the work of adhesion benzene with carbon, 109.33 ergs per sq. cm. In the case of water we note that its work of cohesion is 144.16 ergs per sq. cm.; that this is greater than the work of adhesion water with carbon, 126.82 ergs per sq. cm.

It thus becomes apparent that the following statements are justified: The force of cohesion of benzene molecules for each other is less than the force of adhesion of benzene molecules for carbon. The force of cohesion of water molecules for each other is greater than the force of adhesion of water molecules for carbon.

Work of Adhesion Solid-Liquid vs. Work of Adhesion Liquid-Liquid.—It may be helpful if we compare briefly the methods for the determination of the work of adhesion of solid-liquid systems with that of liquid-liquid systems. Excellent studies on the work of adhesion for liquid-liquid systems have been carried out by Harkins and co-workers.

Consider their data for the adhesional work mercury with water.

Let S_4 = free surface energy of mercury and S_3 for water, as before. Then

$$Wa_{34} = S_3 + S_4 - S_{34}. \qquad (24)$$

Surface tensions S_3, S_4, and interfacial tension, S_{34} can be measured directly in each instance; so in this case all values are determinable in absolute units. At 20° C. for mercury-water a value for work of adhesion of 178 ergs per sq. cm. is obtained; for mercury-benzene the work of adhesion is 148 ergs per sq. cm. This may be compared with analogous values for the carbon-liquid systems. For carbon-water the

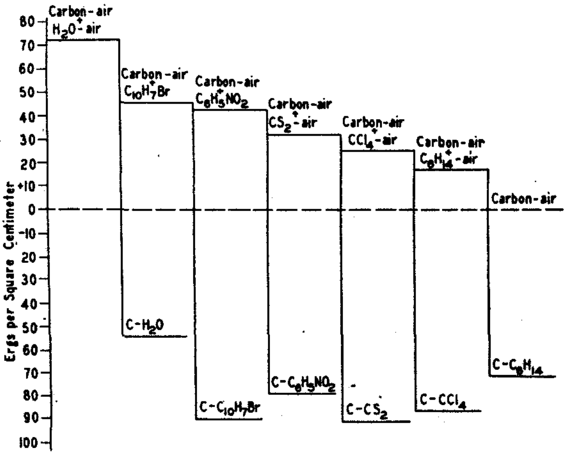


FIG. 4.

work of adhesion is 126.82 ergs per sq. cm.; for carbon-benzene it is 109.33 ergs per sq. cm.

Thus it is to be noted that, contrary to rather general belief, the work of adhesion (also adhesion tensions) of these particular liquid-liquid systems is greater than the work of adhesion (and adhesion tensions) in the solid-liquid, carbon-water or carbon-benzene systems.

In order to bring out clearly the relationship between the values for work of adhesion of some liquids for mercury, and for the work of

adhesion of liquids for carbon, the values for the former, taken from the data of Harkins, are given graphically in Figure 4. They are plotted on the same scale as values for work of adhesion of liquids with carbon, which are given in Figures 3 and 5.

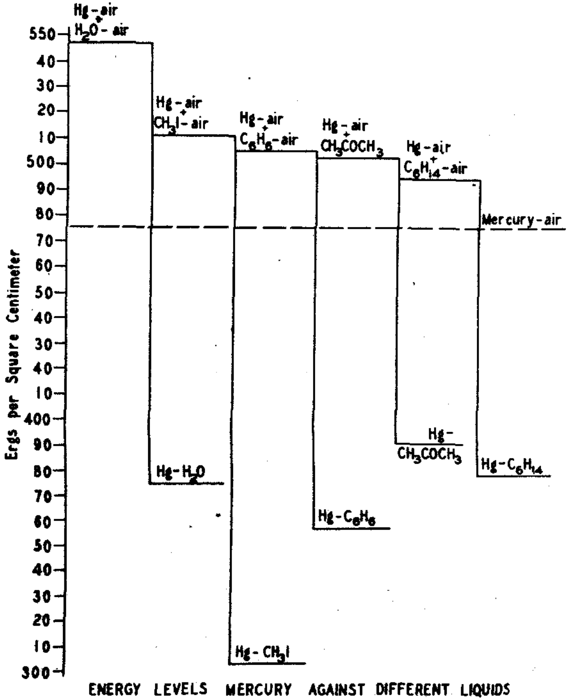


FIG. 5.

The lines extending below the mercury-air base line represent the adhesion tension values for the mercury-liquid systems, and may in fact be taken as indicating the "degree of wettability" of the mercury by the different liquids.

In Figure 5 the work of adhesion values for a number of different liquids and carbon are shown. The total lengths of the lines in each case represent the work of adhesion values. The length of the line below the carbon-air base line (the value of which is taken as the zero of reference) represents the adhesion tension value, and the lower limit in each case represents the energy level of carbon in contact with the liquid in question.

Pressure of Adsorption.—It is believed that the measurement of adhesion tension has thrown considerable light on the question of surface compression in adsorption.

Lagergrin[12] appears to have been the first to suggest that liquids in contact with charcoal were compressed on its surface under pressures of some 10,000 atmospheres. Williams[13] found somewhat higher values and suggested also that the internal pressure of charcoal might reach 58,000 atmospheres. Harkins and Ewing,[14] basing their conclusions upon experimental data obtained in the determination of the apparent density of charcoal, decided that the adhesional pressure between carbon and liquids is more than 20,000 atmospheres in excess of the internal pressures of the liquids.

This conclusion was apparently supported by the work of Lamb and Coolidge,[15] who suggested that the net heats of adsorption of liquids on charcoal are in fact heats of compression and further that all liquids are attracted by the charcoal with substantially the same force. The absolute value of this force was calculated as about 37,000 atmospheres.

Later,[16] Coolidge came to the conclusion that the conception of high liquid compression at the carbon surface was erroneous. Basing his conclusions on the decreasing capacity of the adsorbent with rising temperature, he stated that in none of the cases studied was it necessary to assume an excess pressure of compression as high as 500 atmospheres.

Recently, Howard and Hulett[17] extended some of the earlier work of Cude and Hulett[18] on the determination of the density of charcoal using helium gas; they found values higher than those obtained by Harkins, with even the most compressible liquids. These results indidate that the apparent variations in density of charcoal are due to the difference in depth of penetration of liquid into the pores of the charcoal, rather than to the compressibility of liquid within the pores.

The work in this laboratory on adhesion tension between solid and liquid has shown that the work of adhesion of carbon and water is less

[12] *Bihang till k. Svenska Vet. Akad. Handl.*, **24**, II, 4 (1898).
[13] *Proc. Roy. Soc.*, **98A**, 224 (1920).
[14] *J. Am. Chem. Soc.*, **43**, 1794 (1921).
[15] *J. Am. Chem. Soc.*, **42**, 1146 (1920).
[16] *J. Am. Chem. Soc.*, **48**, 1795 (1926).
[17] *J. Phys. Chem.*, **28**, 1082 (1924).
[18] *J. Am. Chem. Soc.*, **42**, 391 (1920).

than the work of cohesion water for water. On the assumption that the internal pressure of a liquid is proportional to a function of its surface tension [19] we may calculate from the values obtained for adhesion tensions solid-liquid an approximate value for the pressure of adsorption of a liquid on the surface of a solid. The ratio between the pressure of adsorption of a liquid on a solid and the cohesion pressure of the liquid is then the same as that between the work of adhesion, *Wa*, and the work of cohesion, *Wc*. If the internal pressure of the liquid is known, the adsorption pressure solid-liquid is given by the product $Wa/Wc \times$ internal pressure. The values obtained in this way will undoubtedly be quite as accurate as those existing in the literature for the internal pressures of liquids.

In Table 3 a few such values are listed to give an indication of the magnitude of these adsorption pressures. There appear to be no concordant values for internal pressures listed in the literature. Since this table is merely for the purpose of illustration, maximum and minimum values are taken from tables furnished by Edser.[20]

TABLE 3.—PRESSURE OF ADSORPTION OF LIQUIDS ON CARBON.

Liquid	Internal Pressure Atmospheres	Wa in Ergs	Wc in Ergs	Adsorption Pressure Atmospheres	Excess Over Internal Pressure
Water	6375	....	....	5600	— 775
	12450	126.82	144.16	10900	— 1550
Benzene	1890	....	....	3650	+ 1760
	2600	109.33	56.50	5000	+ 2400
Carbon disulfide	2490	....	....	4680	+ 2190
	2620	121.75	64.60	4950	+ 2330
Hexane	1126	....	....	2770	+ 1640
	1713	87.75	35.64	4220	+ 2510

These values are such that it appears that the adhesional pressure between carbon and water is at least 1000 atmospheres less than the internal pressure of water, while even in the case of the most strongly adsorbed organic liquids, the excess of adhesional pressure above the internal pressures of the liquids is not more than 3000 atmospheres.

It therefore seems probable that the high values given by Harkins and others are very much too great.

Orientation of Molecules at Interfaces.—At the present time one of the most interesting fields of colloid chemistry is centered around the study of the orientation of molecules at interfaces.

Hardy [21] was the first to suggest that molecules at interfaces are definitely oriented. He believed that owing to the unsymmetrical field

[19] For references consult Hildebrand's Am. Chem. Soc. Monograph "Solubility," pp. 108-113.
[20] Fourth Brit. Report on Colloid Chemistry, Vol. 4, pp. 89-114 (1922).
[21] *Proc. Roy. Soc. London*, 86A, 610 (1912).

of force surrounding the molecules, adjustment of the molecules at the interface should occur in such a manner as to give an interfacial region of minimum potential energy. Langmuir [22] presented experimental data which tended to confirm this view. Harkins, Davies and Clark,[23] as a result of their experimental work, which was independent of that of Langmuir, advanced practically the same view that molecules were oriented at interfaces and stated that the active groups would extend toward the liquid phase or, in the case of two liquids, the active group would extend toward that liquid most like itself in chemical constitution.

This view has found further substantiation in the work of a number of more recent investigations, including that of Adams,[24] Schofield and Rideal,[25] Sugden,[26] and Frumkin.[27] That molecular orientation actually exists at solid-liquid interfaces is substantiated by the work of Hardy,[28] Constable and Palmer,[29] and Bartell and Miller.[30]

In their work on the adsorption by carbon of compounds in solution, Bartell and Miller have shown that there is good evidence that orientation of solute occurs in such a manner that the less polar or hydrocarbon group is in direct contact with the carbon, while the more polar group extends into the aqueous solution phase.

Adhesion Tension and Adsorption.—The work to date on adhesion tension (which includes considerable data not contained herein) further confirms the conclusions from the work on adsorption. Those compounds which have a structure favorable to high adsorption likewise show high adhesion tension values. It appears that in the case of a polar hydrocarbon substance the molecular orientation is such that the more polar group extends towards the liquid phase. This appears to hold true for orientation at both carbon and air interfaces.

In the case of silica as adsorbent, the situation is different. When a liquid is brought in contact with silica the molecule appears to be so oriented that the more polar group is in contact with the silica. Accordingly, those liquids which give with carbon a high adhesion tension give with silica a low adhesion tension. In case of a polar liquid bounded by silica and air, as would be the situation for such a liquid in a capillary tube, it may be considered that at the air interface the polar ends of the molecules would be directed inward toward the liquid, while at the silica interface the polar ends would be directed outward toward the silica.

We are at present extending our work on adhesion tension so as to obtain additional information relative to the orientation of molecules

[22] *Met. Chem. Eng.*, 15, 467 (1916); *J. Am. Chem. Soc.*, 39, 1848 (1917)
[23] *J. Am. Chem. Soc.*, 39, 541 (1917).
[24] *Roy. Soc. Proc.*, 101A, 452 (1922).
[25] *Roy. Soc. Proc.*, 109A, 57 (1926); 110A, 167 (1926).
[26] *J. Chem. Soc.*, 125, 1167 (1924).
[27] *Z. Physik. Chem.*, 109, 34 (1924); 111, 190 (1924); 115, 485 (1925).
[28] *Proc. Roy. Soc.*, 100A, 550 (1922); 101A, 487 (1923); 107A, 1207 (1925); *J. Chem. Soc.*, 127, 1207 (1925).
[29] *Proc. Roy. Soc.*, 107A. 255 (1925).
[30] *J. Phys. Chem.*, 29, 992 (1924).

at interfaces. Our preliminary work indicates that adhesion tension data will give us a method for determining the results to be expected when an adsorbent is placed in a solution of miscible liquids. Obviously, a liquid which will tend to carry the system to the lowest energy level will be the one which will be most highly adsorbed.

University of Michigan,
Ann Arbor, Michigan.

INVESTIGATIONS ON MOLECULAR SIEVE MEMBRANES

By L. Michaelis

A membrane interposed between two liquids of different composition frequently changes the diffusion of the constituents of the solutions as compared with the diffusion which takes place when the two solutions are brought into direct contact without a membrane. The interference of the membrane may go so far as to prevent entirely the exchange of some of the constituents across the membrane. One may think of two different ways in which such an interference is exerted by a membrane. On the one hand the membrane may be a homogeneous substance representing a distinct phase not miscible with the adjacent solutions and working as a solvent for certain kinds of the dissolved molecules. In this case the permeability of the membrane for different substances will be controlled by the solubility of the different kinds of molecules in the substance of the membrane. On the other hand a membrane may have the structure of a sieve, the pores of which may be filled with the adjacent solutions, while the substance of the membrane itself is inert and is by itself entirely impermeable to the solutions. Certainly there are membranes in which both of these properties are combined, and such membranes may be very important from a physiological point of view, but to understand better the functions of a membrane investigations should begin with a membrane in which one of these two types is realized in a possibly pure condition. This paper deals with the sieve membrane.

The effect of a pure sieve membrane depends largely on the size of the holes. Schematizing a little we may distinguish the following types of sieve membranes: (1) sieve membranes such as filter paper which are impermeable only for large particles; (2) cell filters, e.g., the finest sorts of filter paper which are not permeable for blood corpuscles but are for bacteria; (3) bacterial filters such as clay or kieselguhr filters which are impermeable for bacteria but permeable for colloids in general; (4) colloid filters which are permeable for the so called truly dissolved substances but impermeable for colloids. These are membranes of parchment paper, animal skins, etc., and the usually used collodion membranes. Finally there are molecular sieve membranes which exert an influence even on the diffusion of kinds of molecules of decidedly non-colloidal character, such as sugar, urea, and simple

salts. Among these membranes is the best known one, the copper ferrocyanide membrane of W. Traube, which played a great rôle in the development of the theory of osmotic pressure. The disadvantage of this membrane is that it is very delicate and mechanically little resistant even when imbedded in the frame-work of a clay cell. In order to operate with these membranes, the membrane forming substance, copper sulfate and potassium ferrocyanide, must be present on either side of the membrane. This condition renders detailed investigations very complicated.

Fortunately another type of a molecular sieve membrane has been discovered which can be much more easily handled and used for different investigations. This membrane consists of collodion but it differs from the usually used collodion membrane in the method of preparation. Many investigators have pointed out that the pore size of a collodion membrane depends on the degree of evaporation of the organic solvent in which the collodion has been dissolved.[1] If after a certain period of this evaporation the membrane is wetted by water a stationary condition of the collodion is established and a definite pore size is obtained. Bartell and Carpenter,[2] furthermore Hitchcock,[3] even suggested methods for the measurement of the pore size in such membranes. Bartell [4] and his collaborators showed that several well-measurable properties of the membrane are determined by the pore size.[5] Now when the evaporation of the organic solvent is allowed to continue until practically all of the organic solvent has been removed, a membrane is obtained with such a small pore size that the properties are markedly different from those of the incompletely dried membranes.[6] It is with this kind of membranes that we are concerned in this paper.

There is not sufficient time available today to explain in detail the preparation of such membranes.[7] It may suffice to mention that membranes with properties permanent for many months can be obtained when a membrane is prepared as a plane film on a mercury surface. After partial drying insufficient to remove all elasticity it is sealed on the ground rim of the open end of a cylindric or bell jar-shaped glass vessel by means of a collodion solution. Afterwards it is allowed to reach the completely dried condition by exposure to the air for several days. The diffusion of dissolved substances across such a membrane goes on very slowly and cannot be compared at all even with the most impermeable of the membranes ordinarily used for dialysis or ultrafiltration.

[1] Bechhold, H., *Z. Physik. Chem.*, 60, 257 (1907); 64, 328 (1907); Walpole, *G. S., Biochem. J.*, 9, 287 (1915); Krogh, "The Anatomy and Physiology of Capillaries," New Haven, p. 212 (1922); Bartell, F. E., and Carpenter, D. C., *J. Phys. Chem.*, 27, 101, 252 (1923); Hitchcock, David N., *J. Gen. Physiol.*, 8, 61 (1925-26).
[2] *Loc. cit.*
[3] *J. Gen. Physiol.*, *9* *755* *(1926)*.
[4] "Colloid Symposium Monograph," Vol. 1, p. 120 (1923).
[5] Bartell, F. E., and Van Loo, *J. Phys. Chem.*, 28, 161 (1924).
[6] Michaelis, L. and A. Fujita, *Biochem. Z.*, 161, 47 (1925).
[7] Michaelis, L., Ellsworth. R. McL., and Weech, A. A., *J. Gen. Physiol.*, 10, 671 (1927).

The behavior of the individual membranes varies between certain limits, though the behavior of each individual membrane remains absolutely constant. First of all it was necessary to find a method to characterize the individual properties of a membrane. The following method proved satisfactorily.[6, 8] It is based on the observation that an electric potential difference between two solutions of the same salt e.g. between two potassium chloride solutions of different concentration on both sides of the membrane is established. The reason for the choice of potassium chloride is that no potential difference is established between potassium chloride solutions of different concentrations without a membrane under any circumstances, so that with this electrolyte there is no correction for the elimination of liquid junction potentials. Even membranes with larger pore sizes such as parchment membranes may cause a small potential difference between two potassium chloride solutions of different concentrations. It can be shown also that membranes of a type less studied hitherto may give a smaller or greater effect in this respect. This can be shown in membranes of paraffin, wax, mastic, rubber, which are prepared by impregnating filter paper with these substances.[9] Table 1 shows the potential differences obtained with such membranes between 1/10 *N* and 1/100 *N* potassium chloride solutions.

TABLE 1.—POTENTIAL DIFFERENCES (IN MILLIVOLTS) BETWEEN 0.1 AND 0.01 *M* POTASSIUM CHLORIDE SOLUTION IN DIFFERENT MEMBRANES. (THE MORE DILUTE SOLUTION ALWAYS BEING POSITIVE.)

Parchment paper	10	Collodion membranes:	
Paraffin	13	Usual large pored membrane	5–10
Wax	21	Dried membrane of "gun cotton"	25
Mastic	24	Dried membrane of "celloidin" according to condition of drying	45–55
Rubber	29	Theoretically possible maximum value (including the correction for activity factors of KCl) if the mobility of Cl is zero	55

In any case the more dilute solution is positive. Small potential differences of this kind may be observed also with collodion membranes of the ordinary type. But all these effects are decidedly smaller than in the dried collodion membrane. Here the potential differences according to the individuality of the membranes vary from about 40 to 55 millivolts. There are certain kinds of collodion membranes in which even after a thorough drying process not even 40 millivolts can be

[8] Michaelis, L., *J. Gen. Physiol.*, 8, 33-59 (1925); Michaelis, L., and Perlzweig, W. A., *J. Gen. Physiol.*, 10, 575-598 (1927).
[9] Michaelis, L. and Dokan, Sh., *Biochem. Z.*, 162, 258 (1925).

reached. With the sort of collodion used for most of these experiments values of 52 or even 54 millivolts are very common and rarely they are less than 45 millivolts. These values can be reproduced for the flat bell jar type membrane within some tenths of a millivolt in the same membrane even after months. It will be shown presently that at potential differences of about 55 millivolts the theoretically possible maximum value is reached. Many of these membranes approach this limiting value very closely, others not quite so well. This value may be used as a characterizing feature of an individual membrane and may be called the "characteristic concentration potential" or CoP. Hence CoP is the potential difference between 1/10 and 1/100 N solutions of potassium chloride when separated by the membrane.

Investigation of the diffusibility of dissolved substances in aqueous solutions was started with the non-electrolytes, as here the diffusion is not complicated by electrical forces. On account of the sluggishness of the diffusion across membranes of the last mentioned type, such experiments require a very long time, days and even weeks. At the time when this part of the investigations was being undertaken,[10] the flat form of the membrane representing the most unchangeable type had not yet been developed. It may be that this part of the investigations will require a more thorough study for details. In any event, the main features are so obvious that there is no doubt concerning the general principle. The investigations were concerned only with relative values of diffusion coefficients for one arbitrarily chosen substance taken as a unit. A mixture of this standard substance, usually urea, and of some other non-electrolyte, each in about 1/10 M concentration, was separated by the membrane from pure water and after a suitable time during which not less than 5 per cent but not more than about 10 per cent had diffused, the diffused amounts were determined by analysis. In such a way the diffusion coefficients of a certain number of substances were estimated. The results are shown in Table 2, together with the relative molecular weights of the substances compared with that of urea as unity.

TABLE 2.—RELATIVE DIFFUSION COEFFICIENTS AND RELATIVE MOLECULAR WEIGHTS OF CERTAIN SUBSTANCES IN $M/10$ CONCENTRATION WITH UREA, UREA BEING TAKEN AS UNITY.

	Relative Diffusion Coefficient	Relative Molecular Weight
Methyl alcohol	9.2	0.53
Ethyl alcohol	3.0	0.77
Propyl alcohol	1.0	1.00
Butyl alcohol	0.8	1.23
Glycerin	0.22	1.53
Chloral hydrate	0.11	2.75
Monochlorohydrin	0.067	1.84
Glucose	0.00	3.30

[10] Fujita, A., *Biochem. Z.*, 170, 18 (1926).

Though the accuracy of the figures should not be overrated, it is quite obvious that the speed of diffusion depends on the molecular size or even better on the molecular volume. When the different substances are put in the order of their diffusibility, the order is the same as the one for the diffusion in a free aqueous solution, as far as one can see. But the differences are enormously increased in the case of the membrane, e.g., the diffusion coefficients of methyl, ethyl, and propyl alcohol have a ratio of 9 : 3 : 1. Glycerin shows a very slow diffusion and with sugars no diffusion can be detected at all in any reasonable time. On the other hand, attention should be drawn to the extremely high speed of diffusion of ammonia, which has not been tabulated. The electrolytic dissociation of ammonia is small enough to be neglected for this purpose.

Collander[10a] repeated this kind of experiment. His membranes did not show quantitative differences of quite the same magnitude, probably because his membranes were not quite so efficient. But in principle his results are confirmatory throughout. Again, he pointed out the extreme high speed of ammonia, accounting for it by its exceptionally small molecular size as compared with all other applied substances. But, as will be shown later on, this does not hold for the ammonium *ion.* Ammonia in the applied concentration does not change the membrane chemically, because the membranes used for these experiments did not show afterwards any change in diffusibility for other substances. These observations justify the use of the term molecular sieve membranes for these membranes, as the size of the molecules, even in relatively smaller molecules, is responsible for the diffusion in a high degree. It may justly be surmised that the diameter of the pores may be of the order of magnitude of single molecules.

We shall proceed now to the diffusion of electrolytes across these membranes. The diffusion of such a simple electrolyte as potassium chloride across a dried collodion membrane into pure water goes on with an extreme slowness which is surprising even compared with the diffusion of a non-electrolyte of comparable molecular size. With good membranes no traces of the electrolyte can be detected in the water even after days. The diffusion of potassium chloride is much accelerated if a solution of sodium nitrate is placed outside the membrane instead of pure water. At least the diffusion of potassium proceeds with a reasonable speed, whereas the diffusion of the chlorine is extremely slow even in this case. This observation leads to the conclusion that the diffusibility of the cation is much greater than that of the anion, so that a reasonable speed of diffusion can take place only when the cation can be exchanged for another cation migrating in the opposite direction. The following table shows that this is true in general when 1/10 *M* solu-

[10a] Collander, R. Societas Scientiarum Fennica, *Commentationes Biologicae* 2, No. 6 (1926).

tion of potassium nitrate is separated by the membrane from 1/10 *M* solution of sodium chloride, and after a suitable time the sodium chloride is analyzed for potassium, and the potassium nitrate is analysed for chloride. It can be seen that on the average 10 times as much potassium passed the membrane as chloride. (*See* Table 3.)

TABLE 3.—DIFFUSION EXPERIMENTS WITH GOOD MEMBRANES.
$M/10$ KNO_3 diffusing against $M/10$ NaCl across a dried collodion bag membrane.

Membrane No.	CoP of the Membrane Before the Experiment (In Millivolts)	CoP of the Membrane After the Experiment (In Millivolts)	Time of Diffusion (Days)	Diffused Amount (in 10^{-6} Mols.) Potassium	Diffused Amount (in 10^{-6} Mols.) Chlorine	Ratio K:Cl
1	51	41	3	14.3	4.3	3.3
			6	32.2	3.2	10
			12	67.0	9.2	7
2	53.1	46.5	2	11.6	1.2	10
			4	25.0	1.5	16.6
			8	56.0	2.6	21.5
			12	85.0	5.2	16.3
3	50.2	41.0	2	28.3	5.6	5
			4	63.5	9.4	6.6
			8	150	30	5
			12	214	52	4.1

This holds only when the CoP of a membrane is not considerably less than the possible maximum value. The next table (Table 4) shows an example of experiments with membranes of a sort of collodion which furnish membranes with a much lower CoP. In general the permeability of these membranes also is very poor. Here again each experiment required some weeks to obtain analyzable amounts of the substances. Yet the differences in the diffusion of chlorine and potassium have almost disappeared. From this it can be seen that in fact the CoP has an intrinsic connection with the difference of diffusion of the cation and the anion.

TABLE 4.—DIFFUSION EXPERIMENTS WITH POOR MEMBRANES OF "PARLODION."
$M/10$ KNO_3 diffusing against $M/10$ NaCl.

Membrane No.	CoP (Millivolts)	Time (Days)	Diffused Amount (In 10^{-6} Mols.) Potassium	Diffused Amount (In 10^{-6} Mols.) Chloride	Ratio of K:Cl
1	21.5	8	1.94	2.3	1
2	16.6	26	2.6	2.6	1
3	19.1	26	13.5	8.4	1.6
4	24.3	26	15.8	9.0	1.7
5	23.8	26	23.3	14.0	1.7

If the mobility of the cation and the anion is different within the

membrane it must follow that an electric potential difference will be established across the membrane. In fact the foregoing Table 1 showed such potential differences established with different kinds of membranes between 1/10 and 1/100 *M* solutions of potassium chloride. It may be added that in membranes which show the maximum potential difference for potassium chloride solutions, or which at least approximately reach up to the maximum value, the potential differences between two solutions of the same electrolyte in the concentration ratio 10:1 is always the same and independent of the anion, provided the cation is monovalent. The valency of the anion is of no appreciable importance. The following table shows the electromotive forces of such diffusion chains where the ratio of the concentration is always 1/10:1/100 *M*. (*See* Table 5.)

TABLE 5.—ELECTROMOTIVE FORCES OF DIFFUSION CHAINS.

One of the following electrolytes is present on one side of the membrane in 0.1 *M* solution, and on the other side in 0.01 *M* solution. The more dilute solution is more positive by the following number of millivolts:

HCl	54.8	K_2CO_3	48
KCl	47	$K_2C_2O_4$	48
KJ	48	K Ferrocyanide	49
KBr	47	LiCl	45
KNO_3	45	RbCl	49
K_2SO_4	44	NH_4Cl	47

When the cation is bivalent, the potential differences are very uncertain. A definite report concerning their values must be delayed for a special investigation. In salts of trivalent cations the potential difference is much more distinctly established, but it can be shown that this potential difference does not depend on the concentration of the trivalent cations, but on the concentration of the hydrogen ions which are present as a consequence of the hydrolysis of the salts of trivalent cations. I wish to emphasize that among the univalent cations the hydrogen ions did not play any particular rôle. A diffusion chain with hydrogen chloride behaves almost accurately like a diffusion chain with potassium chloride, sodium chloride or lithium chloride.

When the ratio of the concentrations of the salt present on both sides of the membrane in different concentrations is varied, the potential difference follows approximately the same logarithmic rule as in a regular concentration chain. The potential difference for a concentration, e.g., 1:100, may in the best cases reach 110 millivolts, etc. When the concentration range is varied but the concentration ratio kept constant, the theoretical maximum value is approached better, the lower the concentration range (e.g., for a concentration ratio 2:1 the theoretical maximum value is 17.7 millivolts). Table 6 shows the potential difference obtained when the range of concentration was varied. One example is given for potassium chloride, another for lithium chloride.

TABLE 6.—POTENTIAL DIFFERENCE BETWEEN TWO SOLUTIONS OF THE SAME ELECTROLYTE IN CONCENTRATION RATIO 2:1 IN DIFFERENT RANGES OF CONCENTRATION.

Range of Concentration	Electrolyte KCl	Electrolyte LiCl
0.01 : 0.02 Molar	16.05	15.1
0.02 : 0.04 "	15.4	13.4
0.04 : 0.08 "	13.6	11.4
0.08 : 0.16 "	10.8	8.3
0.16 : 0.32 "	7.3	5.2

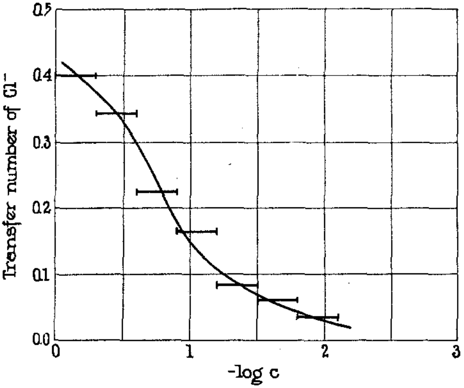


FIG. 1.

Abscissa: Negative logarithm of the concentration of KCl.

Ordinate: Transfer number of chlorine in KCl, as calculated from a diffusion chain consisting of two different KCl solutions separated by the membrane. [The concentration ratio on the two sides of the membrane was always 2:1. Hence the difference of the logarithm of the concentration always 0.30.] The horizontal dashes cover the concentration differences of a single concentration chain. The curve is an interpolation curve for the transfer number of chlorine.

It cannot be doubted that these potential differences are due, for the greatest part, to the difference in the mobilities of the anion and the cation. It may be that some minor factors should be accounted for also in the potential differences. However, it will be shown in a special investigation that the other sources of potential differences can be only very small as compared with the differences of the mobilities. No appreciable error will be made if the whole potential difference of these diffusion chains is attributed to differences of mobilities. If that is

true, the potential difference of these chains may be used to calculate the ratio of the mobilities of the anion and cation, or in other words, to calculate the transfer number for the ions in any electrolyte within the pores of the membrane. As the potential difference between two solutions of the same concentration ratio depends largely on the concentration range, we may infer the surprising result that the transfer number of any electrolyte depends much more on the concentration within the

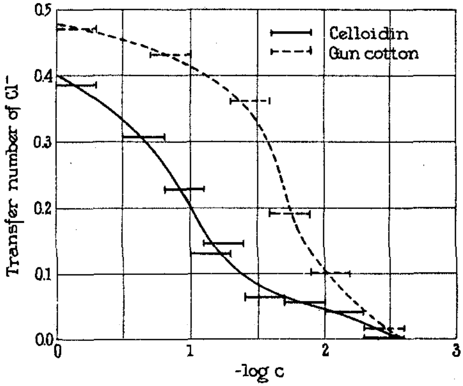


FIG. 2.

Abscissa: Negative logarithm of the concentration of KCl.

Ordinate: Transfer number of chlorine in KCl, as calculated from a diffusion chain consisting of two different KCl solutions separated by the membrane. [The concentration ratio on the two sides of the membrane was always 2:1. Hence the difference of the logarithm of the concentration always 0.30.] The left curve shows the result for a celloidin membrane with an almost maximal CoP, the right hand dotted line shows the same for a gun cotton membrane with a considerably lower CoP.

membrane than it does within a free aqueous solution. Figure 1 shows this fact. The abscissa is the concentration in a logarithmic scale. The horizontal dashes show the transfer number of chlorine in potassium chloride calculated from the potential difference of the diffusion chain in a concentration ratio 2:1. The length of each dash covers the concentration ratio 2:1 which corresponds in a logarithmic scale 0.30 units of the scale. The curve is an interpolation curve for the transfer number for chlorine. It can be seen that the transfer number of chlorine

is almost negligible in 1/100 *M* solution but goes up almost to the value ½ in a molar solution, thus almost reaching the value holding for a free aqueous solution. The course of such a curve is individual for a membrane but the general shape is always the same. Figure 2 shows two such curves for two different membranes.

The transfer number can be determined also by direct electric transfer experiments. The following method might seem to be simplest. In one of the types of apparatus which are used in physical chemistry for the determination of transfer numbers, the anode and the cathode chamber may be separated by the membrane. After the current has been allowed to pass through the system, the change of the potassium chloride contents in the anode and the catode chamber may be determined by chemical analysis. This method is not available however, because the amount of current necessary for reliable results is so large that the membrane would not tolerate the electric current without being irreversibly changed in respect to its properties of permeability. The time is not available to explain these changes in details. This item must be delayed for a further paper, and it is sufficient at the present time to emphasize that only weak currents for a relative short time can be applied. In suitable membranes we succeeded in carrying out a large extended set of such transfer experiments over a period of months without changing the properties of the membrane at all, as judged from the CoP. A solution of sodium chloride was on the one side of the membrane and a solution of potassium nitrate on the other. The direction of the current was chosen so that potassium migrated into the sodium chloride solution and the chlorine migrated into the potassium nitrate. The analysis can be made by micro-methods and the transfer number of potassium chloride thus determined in a direct way. There are some uncertainties involved in this method, the detailed explanation of which would exceed the time available. One of these sources of error is the fact that in general when two successive transfer experiments within a short space of time are duplicated, the transfer number as determined by the second experiment was always a little different from the one determined by the first experiment. This is not the case when a sufficient space of time is left between the two experiments. In such a case the experiments are well reproducible. Obviously a polarization effect is established during the experiment.

Due to the fact that the electric current is flowing across a solution of an electrolyte of which the anion and the cation have different mobilities, an accumulation of this electrolyte must take place on the one side and a dilution on the other side. Therefore while the current is flowing within the membrane, an accumulation of potassium chloride will take place on the one side and a dilution on the other side. Again, since the transfer number here largely depends on the concentration, the transfer number determined by electric transfer experiment is not

necessarily the transfer number holding for the concentration in which the electric transfer experiments had been started. For this reason an absolutely complete agreement between the transfer numbers as obtained by the two methods cannot be expected. Taking into consideration the reasonable limits of accuracy, the agreement of the transfer numbers is good enough to maintain the assumption that the electromotive forces of the diffusion chains in a membrane can be justly interpreted almost quantitatively as due to the difference of mobility of the

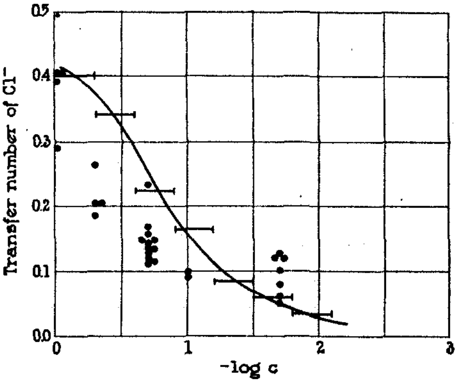


FIG. 3.—The full curve and the dashes have the same significance as in Figure 1. The dots show the results of direct electric transfer experiments.[10b]

anions and cations. The other sources of potential differences which should be interpreted in terms of thermodynamics and not in terms of mobilities, play only a minor rôle. This is certainly very different from the galvanic chains of the type made up with membranes according to Cremer[11] and Haber[12] or by membranes of a homogeneous water-immiscible oily phase in which differences of mobilities are of lesser importance and thermodynamical considerations have to be applied, according to Beutner.[13] Nor does it seem practicable to apply for the collodion membranes those considerations which recently Horovitz[14] used in glass membranes.

[10b] Michaelis, L., Weech, A. A. and Yamatori, A., *J. Gen. Physiol.*, 10, 684 (1927).
[11] Cremer, M., *Z. Biol.*, 47, 1 (1906).
[12] Haber, F., and Klemensiewicz, *Ann. Phys.* [4] 26, 927 (1908).
[13] Beutner, R., "Die Entstehung elektrischer Stroeme." Stuttgart (1920).
[14] Horovitz, Karl, *Z. Physik.*, 15, 369 (1923); *Sitzungsberichte der Akademie der Wissenschaften in Wien*, Abteilung IIa, 134, 335 (1925); Horovitz, Karl and Josef Zimmermann, ibid., p. 355.

Let us proceed now to electromotive forces established between two aqueous solutions of different electrolytes in the same concentration.

Even without a membrane a potential difference is established when, *for example, 1/10 N solution of potassium chloride is brought into contact* with 1/10 *N* solution of sodium chloride, as a consequence of the difference the mobility of the potassium ion and the sodium ion. Yet *the potential differences are much greater when a membrane separates* the two solutions. The membranes with the highest CoP, i.e., with the greatest potential difference between 1/10 and 1/100 *M* solution of potassium chloride give the highest potential differences between two solutions of different salts also. Table 7 shows the potential differences obtained in a membrane with a relatively high CoP. These potentials may be considered as the highest which can be obtained at the present time. The one solution is always a 1/10 *M* solution of potassium chloride. The other solution is a 1/10 *M* solution of some other salt.

TABLE 7.—POTENTIAL DIFFERENCES BETWEEN *M*/10 SOLUTIONS OF POTASSIUM CHLORIDE AND *M*/10 SOLUTIONS OF CERTAIN OTHER ELECTROLYTES.

Solution 1	Solution 2	Potential Difference[1]
KCl	HCl	−93
KCl	RbCl	− 8
KCl	NH_4Cl	− 6
KCl	KCl	0
KCl	NaCl	+48
KCl	LiCl	+74

[1] The sign refers to Solution 2.

TABLE 8.—POTENTIAL DIFFERENCES BETWEEN *M*/10 SOLUTIONS OF HYDROGEN CHLORIDE AND *M*/10 SOLUTIONS OF OTHER ELECTROLYTES.

Solution 1	Solution 2	Potential Difference[1]
HCl	RbCl	+ 87
HCl	NaCl	+140
HCl	LiCl	+165

[1] The sign refers to Solution 2.

In Table 8 the one solution is always a 1/10 *M* solution of hydrogen chloride. It can be seen that approximately the electromotive series may be applied for these potential differences. (*See* Table 9.)

TABLE 9.—COMPARISON OF CALCULATED AND OBSERVED VALUES OF POTENTIAL DIFFERENCE BETWEEN *M*/10 HYDROGEN CHLORIDE AND *M*/10 LITHIUM CHLORIDE SOLUTIONS.

HCl — KCl	93
KCl — LiCl	74
HCl — LiCl, calculated as the sum of both	167
Observed Value	165

On the other hand, two different electrolytes having a common cation never give any appreciable potential difference as can be seen from Table 10.

TABLE 10.—POTENTIAL DIFFERENCES BETWEEN M/10 SOLUTIONS OF ELECTROLYTES HAVING A COMMON CATION.

Solution 1	Solution 2	Potential Difference[1]
KCl	KBr	—2
KCl	KJ	0
KCl	K_2SO_4	—2
KCl	$K_2C_2O_4$	0
KCl	K_4FeCy_6	0
KCl	KOH	—2

[1] The sign refers to Solution 2.

Undoubtedly all these potential differences are brought about in the main part by differences of the mobility of the different cations. A further investigation will have to deal with this problem in detail. We may try to calculate the mobility of the different cations within the membrane. In a free aqueous solution the potential differences between two solutions of electrolytes with different cations and a common kind of anion can be calculated by the formula

$$E = 0.058 \log \frac{u_1 + v}{u_2 + v} \text{ Volts}$$

where u_1 and u_2 are the respective mobilities of the two different cations and v is the mobility of the common anion. If we take the mobility of the anion as negligible we obtain

$$E = 0.058 \log \frac{u_1}{u_2} \text{ Volts}$$

Solving this equation for $\frac{u_1}{u_2}$ we may calculate the ratio of the mobilities of each two cations. In this way we obtain the mobility of the different cations referred to the mobility of potassium as unity. (*See* Table 11.)

TABLE 11.—RELATIVE MOBILITY OF VARIOUS CATIONS REFERRED TO THE MOBILITY OF POTASSIUM AS UNITY.

	Li	Na	K	Rb	H
Relative mobility within the membrane	0.048	0.14	1	2.8	42.5
Relative mobility for a free aqueous solution	0.52	0.65	1	1.04	4.9

Just as in the earlier cases it can be seen that the relative small differences of the mobilities holding for ordinary aqueous solutions are largely increased within the membrane. The ratio of mobility of hydrogen and

lithium in the membrane is almost 1000:1. However, we should not *insist on the accuracy of these calculations as we are not quite sure as* yet in how far the applied formula is accurate for the capillary spaces within the membrane. However, it is unlikely that the principle of these considerations will be essentially changed by those corrections which may become necessary after further investigations.

Johns Hopkins Hospital,
Baltimore, Maryland.

SYNTHETIC KIDNEYS

By Wilder D. Bancroft and R. L. Nugent

The freezing-point of human blood varies between —0.51° and —0.62° under normal conditions, —0.56° being perhaps a standard value. The freezing-point of urine may vary from —0.075° to —5° Relatively small changes in the concentration of the blood may therefore give rise to relatively large changes in the concentration of the urine. The modern view—which is not yet proved satisfactorily—is that the filtration in the glomerulus removes only the colloidal material and causes no change in the relative or absolute amounts of the dissolved substances. On this assumption, the regulation occurs in the tubules, the requisite amounts of water and of dissolved substances passing back into the blood. A mechanism thus exists whereby water may flow from a place of low partial pressure to a place of high partial pressure. So far as the general theory is concerned, it is immaterial whether the concentration or dilution of the urine occurs in one stage or two.

Before we can account for the phenomena, we must develop a theory for the selective concentration or dilution of a solution by filtration or dialysis. Selective membranes may vary from semipermeable ones to ultra-filtration membranes.

Under semipermeable membranes we may distinguish the non-porous ones which owe their semipermeability to selective solubility and the porous ones which are semipermeable because of practically complete negative adsorption. Rubber membranes seem to belong in the first class and copper ferrocyanide membranes in the second. Acetone will go through rubber or dried collodion very rapidly, whereas water does not. At first sight, it seems as though one should be able to filter pure acetone out of aqueous acetone by means of a rubber membrane. If this were to happen, however, we should have a semipermeable membrane with pure acetone as solvent on one side and a concentrated solution of water in acetone on the other side. Acetone would therefore flow through the membrane into the solution, and could be made to flow out only in case the hydrostatic pressure on the solution side were greater than the osmotic pressure. Under a filtration pressure equal

to a few centimeters of mercury pure acetone passes through rubber into a closed vessel *containing liquid acetone.* If a forty-five per cent aqueous solution be placed above the membrane, not only does acetone not filter through, but there is a rapid flow in the opposite direction. In this case a pressure of many atmospheres would be necessary to cause filtration. The lower side of the membrane was not visibly in contact with liquid in these experiments although a film of acetone must always have been present upon it.

A rubber membrane is just as good as a cork to prevent liquid acetone from coming out of a bottle containing aqueous acetone. On the other hand acetone can evaporate from the membrane in case the partial pressure of acetone in the air is lower than the partial pressure of acetone in the aqueous acetone, which it practically always is. It is experimentally quite simple to get practically all the acetone to evaporate through a rubber membrane, whereas not a drop of liquid acetone will filter through into a closed space. If one puts aqueous acetone on one side of a rubber membrane and water on the other, acetone can be detected on the water side in a very few minutes.

A similar line of reasoning applies to a semipermeable membrane of the copper ferrocyanide type. No liquid water will filter through it from a sugar solution unless the hydrostatic pressure is greater than the osmotic pressure; but water will evaporate through such a membrane so long as the partial pressure of the water vapor outside is less than the partial pressure of water vapor in equilibrium with the solution. We have not made these experiments ourselves; but the case is covered satisfactorily by the observations of Ferguson [1] on the behavior of certain molasses puncheons in a very damp cellar. Not only did no liquid water come out of them; but water vapor passed into them until the casks burst from the resulting pressure. Berkeley and Hartley, of course, actually found pressures of the order of one hundred and thirty atmospheres to be necessary to cause negative osmotic flow in the case of their more concentrated sugar solutions.

The matter seems simpler with a porous membrane showing strong positive adsorption and having pores so narrow that there is no unadsorbed liquid in them. The solution in the pores is more concentrated than that outside and it seems at first as though on filtration one should get this more concentrated solution coming through. This is not necessarily the case. In our preliminary work, we have established the "pore size" of certain collodion membranes according to the method employed by Hitchcock.[2] Our results agree with his, and indicate the pores of these membranes to have been of the order of size of those in copper ferrocyanide membranes.[3] We should expect these

[1] *J. Chem. Soc.*, 6, 122 (1854).
[2] *J. Gen. Physiol.*, 9, 755 (1926).
[3] Tinker, *Proc. Roy. Soc.*, 92(A), 357 (1916).

pores to contain nothing but adsorbed liquid. We have further established the adsorption of acetone from dilute aqueous solution by cellulose nitrate and calculated that, in contact with a one-half per cent acetone solution, our membranes should contain a solution several times more concentrated. We have filtered one-half per cent acetone through these membranes under pressures up to half an atmosphere. In no case has the filtrate been of different concentration than the solution. All precautions were taken to prevent evaporation and constant composition was maintained above the membrane by causing approximately five hundred cc. of solution to flow past the membrane for every cc. which filtered through. After each run the filter employed was tested for leaks with congo red solution. These negative results are not surprising. The more concentrated solution in the pores is in equilibrium with the more dilute solution outside the membrane and will therefore be in equilibrium with a solution of the same concentration on the other side. We cannot therefore hope for a change of concentration by filtering through such a membrane except in so far as rapid filtration may force the solution in the pores through without equilibrium being reached or in case the hydrostatic pressure causes a marked change in the composition of the adsorbed liquids. Under any ordinary conditions both these factors are probably negligible. Our general conditions for porous membranes may also be applied to cases of filtration where both compounds of the solution dissolve in a non-porous membrane.

Schmidt [4] found no change in concentration on filtering salt solutions through animal membranes under low pressures. Martin [5] found no concentration effect on filtering dextrose and urea solutions under fifty atmospheres pressure through gelatin and silicic acid membranes. Grollman [6] employing collodion filters, has obtained dilutions up to sixty per cent and believes his results to be due to variations in pore size, some of the pores being small enough to be semipermeable. These results are so improbable that the experiments will have to be repeated in order to determine what important factor, perhaps hydrolysis, has been overlooked by Grollman.

An ultra-filter is a porous membrane which acts like a sieve, stopping some or all of the suspended particles. Since the osmotic pressure of the suspended colloids in a solution is usually small, an ultra-filter may work under a low hydrostatic pressure. As has been stated, the consensus of opinion at present is that the glomerulus acts as an ultra-filter, taking out some or all of the colloidal material, but not producing any change in the relative or absolute concentrations of the substances in true solution.

[4] *Pogg. Ann.*, 99, 337 (1856).
[5] *J. Physiol.*, 20, 364 (1896).
[6] *J. Gen. Physiol.*, 9, 813 (1926).

If the glomerular action is simply ultra-filtration, there would be no appreciable change of concentration of the solutes. Bechhold [7] has considered that glomerular concentration effects cannot be ruled out. He bases this opinion on the fact of preferential imbibition of water from a salt solution by dried animal bladder. There is, however, no necessary relation between the composition of a solution in a membrane and the concentration of the solution that filters through it.

It is now clear that we cannot produce appreciable changes in the concentration of dissolved substances by straight filtration through semi-permeable membranes unless the pressure on the solution exceeds the osmotic pressure of the substances for which the membrane is apparently impermeable, and that concentration changes, due to straight filtration through membranes permeable both to solvent and to solutes, are improbable except under the application of extraordinary pressures. Most organic membranes will not withstand any such pressures and consequently the changes in concentration are not produced by means of straight filtration processes.

The changes must therefore be due to some form of dialysis or electrical endosmose. This conclusion is in accord with the fact that many of the selective membranes in living organisms are bathed by aqueous solutions on both sides. The change in concentration of the glomerular filtrate when passing through the tubules of the kidney is an important case of such selective action where water may actually flow from a place of low partial pressure to a place of high partial pressure, thus involving a change in absolute concentration. Another general type of selective action involves relative rather than absolute concentration effects. The selective concentration of electrolytes in *Valonia* is a striking example of this type of action. With this organism Osterhout [8] found that the ratios of the concentrations of the different ions in the sea-water outside the cell to the concentrations in the cell sap were: Cl, 1; SO_4, 7.1; Na, 5.7; K. 0.025; Ca, 7. There is an enormous relative increase in concentration of potassium inside the cell, and yet the cell wall is evidently permeable both to sodium and potassium ions. The osmotic pressure of the cell sap is practically identical with that of sea-water.

As a first step, we must develop in the laboratory a method of getting such changes in absolute concentrations as occur in urine with a freezing-point varying from —0.075° to —5°, and a method of getting such relative changes as occur in *Valonia*.

Loeb [9] showed that when a solution of acid and salt is separated by a collodion membrane from an acid solution containing no salt but

[7] "Colloids in Biology and Medicine," 2nd edition.
[8] Höber, "Physikalische Chemie der Zelle und der Gewebe," 455 (1926).

having the same hydrogen-ion concentration, a flow of acid may take place from the salt solution to the water solution. He ascribes this to the action of the salt in increasing the diffusing power of the acid, which is not helpful.

Acetone passes readily through rubber while the rate of flow of water and of manganous sulfate is relatively small. Therefore if we

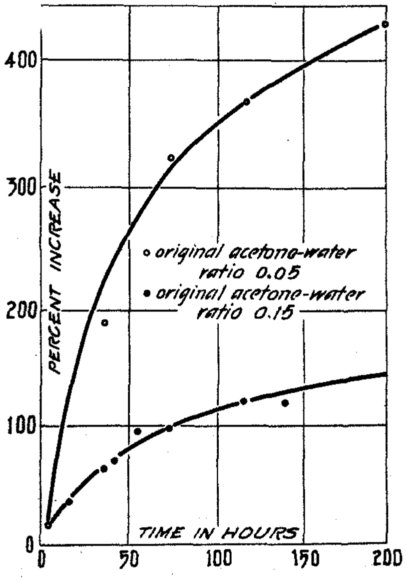


Fig. 1.

start with a rubber membrane in contact with aqueous acetone of the same concentration on both sides and add manganous sulfate on one side, we shall cause a flow of acetone through the rubber membrane to the other side, because manganous sulfate tends to precipitate acetone from an aqueous solution. For example, starting with a solution in which the ratio of acetone to water was 0.15 and adding manganous sulfate to one side until it formed about 20 per cent of the solution,

the acetone-water ratio on the other side was forced up to 0.29 on three days standing, an increase of over 90 per cent. In a similar way an acetone-water ratio of 0.05 was forced up to 0.21, an increase of over 300 per cent. In such experiments, concentration changes on the manganous sulfate side will be less if the volume of that solution is much greater than that of the aqueous acetone. Of course, precautions must be taken to avoid changes due to evaporation.

The accompanying curves (Fig. 1) show the change of this percentage with changing time for the original acetone-water ratios of 0.15 and 0.05. The data are about what one would expect theoretically. Such systems come to equilibrium very slowly. Analyses should really be made to show the acetone-water ratios on the manganous sulfate side instead of making the erroneous assumption that this value remains unchanged.

In the following experiments we employed a number of membranes, placing aqueous acetone solutions of varying concentration on one side and the same water-acetone-manganous sulfate solution on the other side. We could thus bracket the equilibrium concentration as between two solutions, one of which concentrated and the other diluted through the membrane. In this way it was found by Mr. Nugent, who has done all the experiments, that a solution containing 71 per cent water, 12 per cent acetone, and 17 per cent manganous sulfate was in equilibrium with an aqueous acetone solution containing about 32 per cent acetone. The acetone-water ratio on the manganous sulfate side was 0.17 and on the other side approximately 0.47. Similarly a solution containing 64 per cent water, 4 per cent acetone, and 32 per cent manganous sulfate was found to be in equilibrium with a solution containing about 61 per cent water and 39 per cent acetone. The acetone-water ratios were here 0.06 and about 0.63.

Thus if two solutions, in which the acetone-water ratio is 0.17, are separated by a rubber membrane, and if manganous sulfate be added to one side until it forms 17 per cent of that solution, the acetone-water ratio on the other side can theoretically be forced up nearly 200 per cent. If the original acetone-water ratio is 0.06 and if manganous sulfate be added to one side to the extent of 32 per cent, the ratio on the other side should be forced up nearly 1000 per cent. Concentration changes much greater than 1000 per cent can undoubtedly be obtained with this type of system, which is of the general class discussed theoretically by Schreinemakers.[10]

This does not in any way solve the problem of the kidney, because the water that passes back into the blood through the tubules is usually going from a place of low partial pressure to a place of high partial

[10] *Proc. Acad. Sci. Amsterdam* 28, 42 (1925).

pressure as is shown by the freezing-point determinations; whereas the acetone in these experiments is going from a place of high partial pressure (though low concentration) to a place of low partial pressure (though high concentration). We believe that our results are a step forward because we have predicted and have realized experimentally the spontaneous flow of one component from a place of low concentration to a place of high concentration. The principle on which these experiments rest was first stated clearly by Miller.[11]

By means of a "salting-out" mechanism it is easy to show on paper how one could get, as in the case of *Valonia,* a different relative change in the concentrations of two salts both of which pass through the membrane. Suppose we have a membrane which is permeable to water, to potassium nitrate, and to potassium iodide, but impermeable to alcohol. We know experimentally that alcohol precipitates potassium nitrate more effectively than it does potassium iodide. This means that a given addition of alcohol increases the immeasurably small partial pressure of potassium nitrate more than it increases the immeasurably small partial pressure of potassium iodide. Consequently addition of alcohol on one side of the hypothetical diaphragm will cause more potassium nitrate than potassium iodide to pass through the diaphragm away from the alcohol side.

This can be stated more generally. If we have a diaphragm, permeable to water and to two salts but impermeable to a fourth component, we shall have a relative increase of the concentration of salt A on the other side of the diaphragm if the fourth component tends to precipitate salt A more effectively than salt B. If the fourth component tends to increase the apparent solubility of salt A relatively to salt B, there will be an increased relative concentration of salt A on the side of the diaphragm to which the fourth component is added. It is pretty certain that we do not have anything analogous to alcohol in sea-water, which would force potassium salts preferentially into *Valonia,* and the biological chemists do not hold out much hope of there being anything inside the cell which would increase the relative solubility of potassium salts. Consequently, this hypothetical case does not correspond to the actual one of *Valonia* any more than the manganous sulfate case corresponded to the actual one of the kidney.

Osterhout[12] has offered an ingenious explanation for the behavior of *Valonia macrophysa* on the assumption that the protoplasmic membrane of the cell is impermeable to potassium and hydroxyl ions but permeable to molecular potassium hydroxide. Since Osterhout admits

[11] *J. Phys. Chem.,* 1, 683 (1897).
[12] *Proc. Soc. Exp. Biol. and Med.,* 24, 234 (1926).

that the molecular potassium hydroxide dissociates once it has got into the cell, it is hard to see how this hypothesis will account for things if we are dealing with equilibrium conditions. It is superfluous if we are not dealing with equilibrium conditions.

Since the condition of equilibrium for each component which can pass through the diaphragm is that its partial pressures shall be the same on the two sides of the diaphragm, it is impossible for urine to be in equilibrium with blood. To take a single component, the water cannot be in equilibrium unless the freezing-points of the urine and the blood are the same, which is practically never the case.

The concentrations which are reached and which are perfectly definite must therefore depend on the initial osmotic flow and not on equilibrium conditions. Lazarus-Barlow [13] separated equimolecular solutions of sodium chloride, glucose, and urea, and urea from pure water by means of copper ferrocyanide membranes. The initial rates of osmotic flow were not necessarily proportional to the actual osmotic pressures of the solutions. When employing peritoneal membranes of calf, the initial rate of flow into the glucose solution was even greater than that into the sodium chloride solution with an osmotic pressure nearly twice as high. He also pointed out that a temporary osmotic flow may occur between two isotonic solutions, and that an initial flow may even take place from a solution of higher to one of lower osmotic pressure. Lazarus-Barlow [14] further showed that the sodium chloride solution in initial osmotic equilibrium with blood serum is by no means necessarily the one with the same freezing-point and that the strength of this equilibrium salt solution depended upon the protein content of the serum. As any osmotic action in the tubules must be of the nature of initial flow and since much protein is present in the blood bathing the tubules but practically none in the glomerular filtrate, it would seem that any discussion of the physical chemistry of kidney action must include the explanation of these results of Lazarus-Barlow which have been neglected so long.

Since the change of concentration in the kidneys is not an equilibrium phenomenon and since it must therefore be essentially a question of initial flow, it must be to some extent a problem of negative osmosis and that is to be our line of attack. Bartell,[15] among others, has suggested a possible connection between negative osmose and the action of the kidney; but nobody, so far as we know, has pointed out definitely that negative osmose must involve the net transfer of a solution very different in composition from the original one, if it is to account for the

[13] *J. Physiol.*, 19, 141 (1895).
[14] *J. Physiol.*, 20, 145 (1896).
[15] "Colloid Symposium Monograph," 1, 120 (1923).

action of the tubules. The people who have studied negative osmose hitherto, beginning with Graham, have made measurements at times of the volume of the solution transferred; but we have failed, so far, to find any quantitative determination of the composition of the solution transferred. Loeb [16] made the isolated observation that both water and acid diffused out from an acid solution in one case of negative osmose, and that the concentration of acid in the solution decreased continuously. He also observed that the rate of diffusion of acid from the solution was practically proportional to its concentration.

In the Cornell laboratory J. W. Houck has repeated the experiments of Graham [17] on the negative osmose of oxalic acid solutions, using one, five, and ten per cent concentrations and membranes of steer's bladder. We have also determined the net concentrations of the solutions diffusing through the membrane and find that they are three to four times the concentration of the initial solutions in every case investigated. The approximate constancy of these results agrees with Loeb's observations that the rate of diffusion of the solute is proportional to the concentration in cases of negative osmosis. The general facts as to concentration which we have observed with steer's bladder are in accord with those observed by Loeb with gelatin-treated collodion. It seems reasonable to assume that, in the case of negative osmose, the net outflowing solution usually has a different concentration from the initial concentration. We have not found a case in which the net outflowing solution is much more dilute than the initial solution; but there seems to be no theoretical impossibility about this and we have obtained such results with electrodes and an external source of current. If we can find a solution and a membrane such that slight changes in acidity change very much the concentration of the outflowing solution, we shall have gone a long way towards getting a satisfactory working theory of the kidney.

The general conclusions are that straight filtration plays little or no part in effecting the changes in concentration actually observed in the urine, and that these concentration changes do not correspond to equilibrium relations. "Salting-out" effects, negative osmose, initial osmotic flow, and the special nature of the membrane are probably important factors; but we cannot at present say to what extent they enter in. In so far as negative osmose is an electrical phenomenon, it would seem to involve the Donnan equilibrium. Of great importance is the fact placed on record by Osterhout that the two sides of the *Valonia* cell wall are different electrically.

As we see it, our duty as colloid chemists is to suggest possible

[16] *J. Gen. Physiol.*, 1, 717 (1918-19) *et seq.*
[17] *J. Chem. Soc.*, 8, 43 (1856).

mechanisms, which the biologist will examine critically and reject, until we can suggest one which seems to describe the facts with sufficient accuracy. It is in this spirit that this preliminary report is made.

Cornell University,
Ithaca, New York.

THE CHEMISTRY OF BODY PROCESSES

THE NATURE OF THE ACTION BETWEEN GELATIN AND ELECTROLYTES

By A. L. Ferguson

Before considering the subject mentioned in the title of this paper, I wish to submit a somewhat extensive introduction in order to make clear my point of view upon some fundamental questions in colloid chemistry which have a most direct bearing upon the subject. All who have followed the developments in colloid chemistry realize the unsatisfactory condition of the literature. The "facts" of one investigator contradict the "facts" of another. One authority considers an extensive series of investigations worthless, while another authority considers them epoch-making.

Physical-chemical methods have been employed, for the most part, to investigate colloid phenomena, but much of the work has been done by others than physical chemists; their results have appeared largely in physiological, biological, medical, and trade journals. Many of the investigators in these fields are accustomed to qualitative methods and when they use the quantitative methods of physical chemistry there is a tendency to be satisfied with qualitative results. Work is turned out in a few weeks that a physical chemist might take a year or two to complete. The result is the production of an enormous amount of literature of uncertain value. Ostwald said more than ten years ago that it was not possible for a man, even at that time, to follow all the developments.

The topic which I wish to consider in this introduction, however, is not particularly this somewhat unsatisfactory condition of colloid chemical literature, but the general attitude assumed by many investigators of colloid phenomena in their approach to the subject. The indications point strongly toward a deliberate attempt to build a kind of Chinese wall around what they choose to call the field of colloid chemistry. Much energy has been and is being spent to demonstrate that in this field of colloid chemistry new forces of some mysterious nature are at work. The impression is given that one who enters must leave behind him all the working tools of classical chemistry and be prepared to develop new methods of attack and to interpret his data in terms of new principles and a new language, and develop a set of new theories and

generalizations. In this new field one should not talk about solutions and the great mass of laws, principles, and theories developed in connection with them; one must not mention chemical reactions and the quantitative relations which they imply; chemical forces and chemical energy must be displaced by surface tension and adsorption or some other even less understood concepts; the terms atoms, molecules, chemical compounds and solute must be dropped from the vocabulary of one who would be a colloid chemist, and in their places must be substituted such terms as adsorption complex, micelle, dispersed phase, etc.

This attempt at isolation and segregation of so-called colloid phenomena from classical chemistry is, in my judgment, fundamentally un*scientific and unwarranted by the facts. It is unscientific* because the outstanding objects of science are simplification, coordination, unification, the expression of facts and information in terms of well known and well established laws, formulas, generalizations and theories. Even the colloid chemists who are attempting to build this wall admit that a large portion of the phenomena in colloid chemistry may be satisfactorily explained on the basis of the principles of classical chemistry, but since these phenomena may be explained also in terms of their own newly developed language, they choose the latter. In so doing they adopt the attitude of the secessionist. Instead of working for unity and harmony and simplicity, they are developing dissension, segregation and disunion.

The first outstanding colloid chemist was Thomas Graham, whose principal works[1] appeared between 1861-64. Graham came to the conclusion that there was a large number of substances which behaved in a strikingly different manner from the *ordinary* chemical substances and that they required methods of study of their own. To put it in his own words, "Crystalloids and colloids appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between material of a mineral and material of an organized mass." This, or a similar statement, is quoted in practically every book on colloid chemistry from his time to the present. Graham here set the tune to the music of which colloid chemists have been dancing ever since. These authors have either failed to study Graham's works carefully, or have deliberately omitted other statements by him which materially qualify the above. That there is no sharp line of demarcation between colloids and other substances was perfectly evident to Graham. It is frequently stated that, according to Graham, colloids do not diffuse; but his own statement is "Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa are the most serviceable in distinguishing them from crystalloids." In another

[1] *Phil. Trans.*, **151**, 183 (1861); *J. Chem. Soc.*, **15**, 216 (1862); and **17**, 318 (1864).

place he states that tannic acid *passes through* parchment paper about 200 times slower than sodium chloride; gum arabic 400 times slower. In discussing solutions of crystalloids and colloids he states "The phenomena of solution of crystalloids *probably all appear* in the solution of colloids, but greatly reduced in degree." In another place he states, "Ice itself presents colloidal characteristics at or near its melting point. . . . Ice further appears to be of the class of adhesive colloids." In yet another place, "A similar extreme departure from the normal appears to be presented by a colloid holding so high a place in its class as albumin. In the so-called blood crystals of Funke, a soft and gelatinous albuminoid body is seen to assume a crystalline contour. *Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute.*"

What are the distinguishing characteristics of colloids, the properties that have been used as the basis for the division of substances into colloids and crystalloids? Graham gave four such properties: (1) Colloids show extremely slight diffusion, or, as some of the modern chemists prefer to put it, practically no work is required to separate a colloid from its solvent; (2) colloids are unable to penetrate certain membranes; (3) colloids are two-phase systems, or, in other words, colloids do not form true solutions; (4) colloids are unable to appear in the crystalline form.

As I have previously stated, the contention of the colloid chemists that colloids are inherently different from other substances is not warranted by the facts. Some of my reasons for taking this stand will now be submitted.

Property Number 4 above, as a distinguishing characteristic of colloid substances, was completely eliminated by Von Weimarn [2] and others. One of the greatest advances made in colloid chemistry is the result of this work of Von Weimarn, in which he demonstrated conclusively that it is not a matter of some substances being inherently colloidal and others crystalloidal, but rather simply a question of physical state which may be assumed by any substance under certain conditions. By the application of definite principles he converted several hundred crystalloid substances into colloids, among them being such compounds as sodium and potassium chlorides. He placed this portion of colloid chemistry on a strictly scientific basis.

The third distinguishing characteristic mentioned above, that colloids are two-phase systems, was first introduced by Ostwald, later extensively developed by Zsigmondy and Perrin, and since then given great prominence by colloid chemists in general. The distinction made between colloid solution and true solution is that in the former the dispersed phase exists in the form of extremely small masses and consti-

[2] "Grundzuge der Dispersoidchemie," Dresden, 1911.

tutes a separate phase, while in the latter the solute exists in the form of single molecules.

On the basis of this conception of colloid solutions is built probably the most far-reaching theory used in colloid chemistry, i.e., the theory of adsorption. Adsorption and surface forces are to colloid chemistry what chemical reactions and chemical forces are to classical chemistry.

At first there was a distinction drawn between suspensions and colloids based upon the maximum resolving power of the microscope. This was also the distinguishing factor between homogeneous and unhomogeneous solutions. In 1903 Zsigmondy invented the ultramicroscope, which made it necessary to change the classification in some manner. The original division line, i.e., that given by the microscope, was retained as the distinction between suspensions and colloids. The new limit of visibility, established by the ultramicroscope, was arbitrarily taken as the border between colloid solutions and true solutions. However, a homogeneous solution had to be redefined; it now became one in which the particles could not be seen in the ultramicroscope.

This served the purpose well until about 1907, when Bechhold invented his ultra filter. By means of ultra filters he was able to separate from solutions substances much smaller than could be seen by the ultramicroscope. In fact, he could remove many crystalloidal substances of perfectly definite and known compositions, and known molecular weights, which behave in all respects as true solutions. This made it necessary to again redefine a homogeneous solution and to attempt to establish a new line of division between colloid solutions and true solutions.

The line of distinction is now drawn by some on the basis of whether the material is dispersed as single molecules or whether it is made up of aggregates of molecules. On this basis, of course, it must be admitted that even water, and probably the majority of chemical compounds in solutions, must be considered colloid solutions; also that these substances change from colloid to true solutions with changes in temperature and concentration. The inevitable conclusion is that there is no distinction between colloid solutions and true solutions. So far, then, two of the four reasons for the building of an impenetrable wall around the field of colloid chemistry have been shown not to exist.

The second argument, i.e., that colloids are unable to penetrate certain membranes, is also met in the discussion just presented, since this is a property of crystalloids as well as colloids; it is simply a question of the characteristics of the membrane and not the solute or dispersed material.

In connection with this two-phase conception of colloid solutions,

many maintain that such a two-phase system is proven in the case of colloids by the Tyndall effect. There is, of course, no grounds for this distinction, because it has been shown recently that by the proper apparatus the Tyndall effect is exhibited by any ordinary molecular solution.

Concerning the remaining reason for a separation of colloids from other substances, i.e., that colloids do not diffuse or, in other words, do not show osmotic pressure, etc., little need be said. It has been clearly demonstrated that colloids do diffuse. Sorensen[3] in 1917 showed that colloids do exert osmotic pressures and of the order of magnitude commensurate with their molecular weights and concentrations. Einstein[4] pointed out that the kinetic theory demands that colloidal solutions and even suspensions must show osmotic pressures and that particle weights could be calculated from such measurements if they could be accurately made. Zsigmondy[5] measured the osmotic pressures of gold sols. From his measurements he calculated the average particle size and found good agreement between the calculated value and that determined by the ultramicroscope. In fact many molecular weight determinations have been made by the osmotic pressure method upon colloid solutions in which weights were determined from about 100,000 down. These molecular weights were found to be constant and reproducible and to agree well with molecular weights calculated by other means. Among these investigations may be mentioned the work of Hiifner and Gansser[6] on hemoglobin; of Sorensen[7] on egg albumin; of Biltz[8] on a number of dextrins and an albumin from horse serum; and of Bayliss[9] on Congo red. In many of these cases it was found that the osmotic pressure increased proportionately to the absolute temperature, which showed that the effects were purely osmotic.

What more evidence is necessary to show that the stand taken by colloid secessionists is not substantiated by the facts? Undeniable experimental data, backed by reliable mathematical calculations, demonstrate that for every phenomenon where accurate data is obtainable, absolutely no discontinuity is found when materials of gradually increasing molecular weights from universally admitted true solutions to the so-called colloidal solutions are used.

Some raise the objection that the expression "molecular weight" loses its chemical significance. This is probably true, but we might ask whether it has ever really had the significance we have read into it. It has always been a statistical quantity. What meaning has the

[3] *Compt. rend. trav. Lab. Carlsberg,* 12, 1915-17.
[4] *Ann. Phys.,* 4, 17, 549 (1905).
[5] "Kolloidchemie." p. 406 (1920).
[6] *Engelmann's Arch. f. Physiol., Physiol. Abt.* 1907, p. 209.
[7] *Z. physiol. Chemie,* 106, 1 (1919)
[8] *Z. physik. Chemie,* 83, 683 (1913); 91, 705 (1916).
[9] *Proc. Roy. Soc.,* 81B, 269 (1909).

molecular weight of sodium chloride, either in the form of a solid or a solution? A few years ago we wrote the formula for water, H_2O, silver chloride, AgCl, mercurous chloride, HgCl, and ferric chloride $FeCl_3$; now these formulas are written $(H_2O)_n$, Ag_2Cl_2, Hg_2Cl_2, Fe_2Cl_6. The molecular weight of sulfur may have any value up to at least S_{16}. Triethyl sulphonium iodide $(C_2H_5)_3SI$ dissolved in chloroform shows molecular weights all the way from that given by the formula to twelve times that value, depending upon the concentration. In all cases, equally as much in true solutions as in colloid solutions, *our methods for determining molecular weights in solutions give us the weights of the particles.* These may consist of one molecule or a thousand; therefore this is no legitimate reason for not considering colloid solution as true solution.

Recently the distinction between colloid solutions and true solutions has been based upon equilibrium considerations. It is claimed that colloid solutions are unstable, since surface tension tends to cause them to flocculate, and that they must be forced into solution at the expense of energy. Certainly this is not true for the great mass of hydrophil colloids; these substances go into solution as readily as any chemical compound and show reversibility. Even many hydrophobic colloids—when some proteecting colloid has been added—come out and go into solution reversibly. In fact, the statement that colloid solutions are unstable is open to question, even in the case of unprotected hydrophobic colloids. It is true that surface tension tends to cause flocculation, but the very existence of these colloids means that the surface tension force has been balanced by electric forces and such a system is in equilibrium. Of course, if the charges on the particles are removed, precipitation results, but so long as the charges remain there is equilibrium. Any number of instances might be cited in which surface tension tends to produce a change in the system, but other counteracting forces partially overcome the force of surface tension and the whole system remains in equilibrium.

The conceptions of surface forces and adsorption are being worked to their utmost by colloid chemists. One of the stock illustrations given is that a 1 cm. cube of material when reduced to particles of colloid dimensions has its surface area increased from 6 sq. cm. to about 6,000 sq. m. Of course it is evident that a small surface force manifest on the centimeter cube would become a tremendous force after the material had been dispersed to form a colloid solution and the adsorption produced by the centimeter cube would become immensely greater in the colloid solution. But why stop at this particular stage of subdivision; why limit this idea to colloid solutions? A force which increases so markedly in intensity as the material becomes subdivided into smaller and smaller particles should reach its maximum only in molecularly dispersed or

ionized solutions, i.e., there should be maximum adsorption in true solutions. Yet these ideas of surface forces on molecules and adsorption on the surfaces of molecules have, so far as I know, never been considered in connection with reactions in true solutions. Why this abrupt disappearance of forces at an arbitrarily established border line between colloid and true solutions, when they were gaining such headway the nearer they approached this border? It seems to me we must conclude that these surface forces, which we must of course admit are present on all surfaces large or small, are of precisely the same type as that causing ordinary chemical reactions; it is a matter of intensity and not kind.

This point of view is expressed by Langmuir [10] in the following statements. "Reasons have been given for believing that all the forces acting between atoms (or group molecules) in solid bodies are fundamentally similar in character and are of the nature of so-called chemical forces. Thus evaporation, condensation, solution, crystallization, adsorption, surface tension, etc., should all be regarded as typical chemical phenomena." "All the interatomic and intermolecular forces involved in the structure of matter are chemical forces."

"The absence of stoichiometric relations, therefore, is not to be regarded as evidence that the forces involved are not chemical in nature. It is merely the result of purely geometrical factors."

Somewhat the same attitude is expressed by T. Svedberg [11] in the introduction to his book on colloid chemistry. "Colloid chemical treatment of certain phenomena is often regarded as contradictory to, e.g., the pure chemical or the electro-chemical treatment. We often hear people speak of the colloid chemical theory of adsorption in contradistinction to the purely chemical theory; and of the colloid chemical theory of proteins in contradistinction to the chemical or electro-chemical theory of proteins. To a certain extent this is only a quibble about words and terms. Traced to their very sources, all forces chemical, colloid chemical and physical are electrical in nature and therefore both physics and chemistry deal with the same forces—the attractions and repulsions between electrons and positive nuclei. This does not hinder us from dividing the vast field into practical domains of cultivation according to methods used for the work. Colloid chemistry is such a domain. *The colloid chemist must not forget, however, that his science does not operate with any specific forces or substances and that the colloid phenomena traced back to their sources are built up of ordinary physical and chemical phenomena.*"

Again, therefore, we find that no inherent distinction can be drawn between colloid and true solutions. No doubt but what many of the

[10] *J. Am. Chem. Soc.*, *39*, *1848* (*1917*).
[11] "Colloid Chemistry," Chemical Catalog Co., New York, 1924.

phenomena exhibited by colloids may be explained in terms of the language of colloid chemists, but most of them may be explained also in the language of classical chemistry. Is it not more logical, reasonable, and scientific to accept the chemical explanation in all instances where such an explanation is possible and where it is not possible simply to withhold judgment until it is demonstrated that a chemical explanation cannot be satisfactory? Why go out of our way to explain these phenomena on the basis of so indefinite, uncertain, and little understood conceptions as those used by many colloid chemists.

Please do not gain from these remarks the impression that I would discontinue colloid chemistry; that would be as absurd as it would have been seventy-five years ago for someone to have advocated the discontinuance of organic chemistry. At that time there was even a wider gulf between organic chemistry and classical chemistry than the colloid chemists would have today between colloid chemistry and classical chemistry. The gulf between organic and inorganic chemistry has been effectively bridged now, and the one dug by the colloid chemists will eventually be filled. But even after complete harmony is established between the adsorption and chemical views substances of large molecular weight and also substances while they are temporarily existing in a highly associated condition will be best studied in a group by themselves under the subject colloid chemistry.

Having presented my point of view upon some of the fundamental questions in colloid chemistry, I shall now proceed to discuss the topic mentioned in the title of this paper, the chemistry of body processes. From this introduction the reader may understand why I speak of the *chemistry* of body processes, rather than the colloid chemistry of body processes; and no more convincing proof can be offered that reactions between colloids and between colloids and electrolytes are chemical in nature than the reactions which go on in life processes.

During the last few years there has been a pronounced tendency to renew the intimate relation between chemistry and medicine which was first established by Paracelsus during the early part of the 6th Century. Paracelsus was a professor of medicine and maintained that the object of chemistry was to make medicine, not gold. He maintained that the fluids and tissues of the body are chemical compounds, that body processes are chemical reactions and sickness results when these reactions become abnormal, and the normal condition can be restored by the use of proper chemicals. No better statement of the rapidly growing new conception of body processes can be made than this one of Paracelsus, submitted about four centuries ago.

The preachings of Paracelsus resulted in what is known as the age of iatrochemistry, during which many medical schools were established and chemistry was taught by members of the medical faculty.

The prime object of chemistry was to assist in the development of medicine.

In time chemistry assumed more and more the nature of an exact and quantitative science and began to serve the industries, while medicine developed largely along the lines of anatomy and biology, assisted primarily by the introduction of the microscope. From then until recent years the association between chemistry and medicine has been extremely slight. Since the time of Pasteur, however, they have been again approaching each other at a greatly accelerated rate. In a recent address Dr. W. J. Mayo [12] remarked that "The epochal studies of the chemist physician, Pasteur, have been of greater service to mankind than those of any other known human being."

During the last twenty-five years the assistance which chemistry has rendered to medicine is one of the outstanding developments in science. The fundamental work of Emil Fischer on the chemistry of sugars made possible the recent advances in the knowledge of metabolism of carbohydrates. His remarkable work on the chemistry of amino acids and their synthesis into polypeptides laid the foundation for a study of the chemistry of proteins and their digestion and metabolism.

The new science of chemotherapy originated by Paul Ehrlich is coming to dominate medical thought. In an article [13] entitled "Paul Ehrlich's Justification of the Capture of Medicine by the New Chemistry" it is stated that "more immediately practical than any other scientific development of our time is the subjection of the science of medicine to the principles of chemistry. The importance of regarding medicine as a branch of chemistry and not as an independent science is manifest when we remember the therapeutic mysteries for the solution of which mankind is now desperately groping." Among these problems to be solved by the chemist are mentioned cancer, tuberculosis, sclerosis, and diabetes. The last has already been largely solved since the above article was written by the work of Banting on the isolation of the pure principle from the secretions of the pancreas which is responsible for sugar metabolism.

In chemotherapy the exact, quantitative, scientific principles of chemistry are applied to prepare pure chemicals which will cure specific diseases without undue injury to the body cells. The importance of this new phase of chemistry is evidenced by the enormous literature on the subject. During the past year there appeared a book of more than one thousand pages by Professor J. A. Kolmes of the University of Pennsylvania on the "Principles and Practice of Chemotherapy." A few quotations from this book indicate the close correlation being developed between chemistry and life phenomena.

[12] *J. Am. Med. Assoc.*, **84**, 1465 (1925).
[13] *Current Opinion*, **55**, 256 (1913).

"It will be observed, therefore, that a special and selective affinity or combining power of the chemical agent or drug for the parasite is the predominant thought in modern chemotherapy."

"There is a greater need, therefore, for more investigation along these fundamental lines with the hope that accumulated data and experience will gradually establish the nature and mechanism of the selective affinity of chemical agents for parasites (parasitotropism) and for the body cells (organotropism) and the relation between these properties and the chemical constitution of the compounds."

"Unfortunately, there are but very little data available bearing upon what I believe is an important subject in chemotherapy, namely, the affinity of chemical compounds for the protoplasm of parasites and body cells as influenced by the chemical constitution of the latter."

"Complex chemical and physico-chemical forces are involved in the effects of a chemical agent on both body cells and invading parasites, and the matter of selective destruction of parasites in the tissues would appear to be one of chemical or physico-chemical interaction between the chemical agent and protoplasmic constituents of the parasites, just as the specific immunological processes of the body are being gradually placed on the same basis."

The development of this chemical point of view of immunological processes referred to in the last quotation is well represented in the book published two years ago by H. G. Wells of Chicago University entitled, "The Chemical Aspects of Immunity." The introductory paragraph reads as follows:

"Immunological reactions, the processes by which the living organism defends itself against the chemical attacks of the enemies and so is able to exist in an environment seething with such enemies, are chemical reactions. The reagents involved are substances endowed with active chemical properties, and they are the product of chemical activity of the tissues of the body. In few if any cases do we know the chemical constitution of either the poison of the parasite or the defensive agent of the host, and our knowledge is gained entirely by observing the reaction or the effects resulting from the reaction. Therefore, the chemistry of immunity is on quite the same plane as the chemistry of the enzymes, and our lack of exact knowledge, coupled with the vitally important nature of the processes concerned, makes all the more stimulating the investigation of the unanswered problems."

Through a logical and scientific development of the subject, Wells comes to the conclusion that, "Immunological specificity is dependent on chemical individuality" and "the immunological differences between proteins are usually, and as far as now known, always, associated with and presumably dependent upon chemical differences which can be detected by chemical or physical methods." Many illustrations are given to justify this conclusion.

In the quotation above, Wells compares the state of the chemistry of immunity to that of enzymes. The latter is thoroughly discussed in a book by Dr. K. G. Falk of Harriman Research Laboratory, Roosevelt Hospital, published in 1921, entitled "The Chemistry of Enzyme Actions." In the preface Falk states, "Enzyme actions may be treated as a group of chemical reactions analogous to other chemical changes. The substances taking part in such actions are an integral part of chemical science." Throughout the book the reactions which take place within the body, those between colloids as well as others, are all considered as *chemical reactions amenable to the same laws and principles as the reactions of classical chemistry.*

In connection with this paper as a whole, some of the other remarks of Dr. Falk are pertinent. For instance he states, "Another set of phenomena which has given rise to much discussion, especially in recent years, is included under the general topic of "Colloid Chemistry." Colloids are obviously of importance in connection with the study of substances obtained from living matter. *The point of view which will be adopted here is that colloids as chemical substances will be considered in the same way as other substances, and that colloidal solutions will be assumed to possess chemical properties fundamentally similar to those of other solutions.* If apparent exceptions occur, or if phenomena predominate which are more in the background with the non-colloidal substances and solutions whose relations have been studied over a longer period of time, *these exceptions and phenomena will not be designated by new names or branches of science,* but will be retained under the group of relations which have not as yet been developed satisfactorily and which require further quantitative study." In another place he stated, *"Similarly, adsorption compounds will be considered to be fundamentally chemical in character.* Because of such facts as amount of surface involved and physical state of subdivision of the reacting components, the laws of definite and multiple proportions cannot in most cases be proven to apply to the masses in equations, and equilibrium between all of the various components may not be attained in many cases. *The evidence which is rapidly accumulating indicates that chemical compounds are formed with limitations as to their extent just referred to, and that the same general laws of combination exist here as with other chemical compounds."* After presenting the views of some internationally known authorities on the subject of adsorption and surface forces, he remarks, "These views are presented as they show the trend which the studies on adsorption and surface actions are taking. *The general conclusion appears to be that the forces acting are chemical in character and must be treated in the same way as other chemical actions."*

Chemistry so far has been of greatest service to medicine along the lines discussed above, i.e., in the synthesis, through the application of

the fundamental chemical principles, of pure chemicals which may be used to combat in a specific manner certain diseases; or chemicals which are the same as those produced by the glands and organs of the body and which, therefore, may be used in cases where these glands and organs are not functioning properly. Equally important has been the work of the chemist in isolating and obtaining in pure form the principles contained in body secretions. In some instances the exact chemical composition has been determined but in most cases this is still a problem for the future. Another great service rendered by the chemist is in the purification and perfection of many naturally occurring drugs, such as cocaine, quinine, strychnine, morphine, etc. Many of these substances produced ill effects as well as the desired results. The chemist analyzed the materials, located the parts of the molecules responsible for the ill effects and altered them so that only the desired qualities remained. But the work of the chemist along these lines has only started. Nothing is known concerning the chemical composition of most of the body fluids, secretions from glands, enzymes, toxins, antitoxins, vaccines, etc. Undoubtedly only an extremely small amount of the really active principle is contained in vaccine serums and materials of that general class. The contamination introduced into the patient frequently produces serious results. What an opportunity the chemist of the future has to isolate, analyze, and ultimately to prepare synthetically the pure chemical compounds contained in these serums.

Mention, of course, must be made of the remarkable work in identification and partial isolation of those chemical principles so essential to the proper functioning of life processes, known as vitamines. Further discussion of this important field, however, will not be given here, except to state that I believe sincerely that vitamines will ultimately be shown to be pure chemical compounds, that they will be prepared synthetically in the laboratory and that they will be found to react chemically with other chemical compounds within the body.

That the development of chemistry towards the field of medicine has progressed in great strides is certain; also, the benefits derived by humanity as the result have been remarkably great; but even so, work in this direction has just started. So far the greatest instrument brought to the assistance of the various divisions of medicine is the microscope. The cell has been, with minor exceptions, considered the unit, mainly because the microscope was not able to carry them to smaller units. The limit for the development of medicine by this instrument or any other mechanical instrument has been nearly reached. So far no really fundamental knowledge of body processes has been produced by the medical profession. It has done remarkable things considering the limitations of its methods, but before any really fundamental information can be obtained it will be necessary to investigate within the cell

itself. It is here that the greatest work of the chemist is located. The tools and methods of the chemist enable him to start at the point where the medical man is forced to stop; the methods of the chemist are exact and quantitative.

The cell is too large a unit for the chemist to handle; he reaches within the cell to work with the hundreds of different compounds found there and the millions of individual molecular units all alike for each compound. Then he takes these molecules that are all alike and dissects them into their respective building blocks, the atoms of the elements; but even this does not furnish him with the necessary information to explain the reactions which take place so he dissects each of the different kinds of atoms into its universe of protons and electrons, and through the arrangements and movements of these ultimate units in the atom universe he may be able to explain body processes.

It must be remembered that the living body is only a machine absolutely unable to generate energy; it can only transform energy. It is different in a fundamental respect, however, from most machines in that it is self-repairing and self-perpetuating. These things are true not only of the body as a whole but of each of the individual cells. The body is said to be made up almost entirely of colloids. This is probably true, but at the same time no chemicals with which the chemist deals in the laboratory are more specific and definite and permanent in their composition than the thousands of chemicals which go to make up the different parts of the different tissues of the body. Remember also that all of these pure chemical compounds are constructed within the body out of the lifeless food we eat and the air we breathe, by the thousands of individual chemical laboratories within the body. We are told that the food also is mostly colloidal. What more conclusive evidence is needed to demonstrate that the reactions of colloids are strictly chemical and that perfectly definite compounds result from these reactions? Life and growth consist in the continuous process in which precisely the same chemical compounds, be they colloids or otherwise, enter into precisely the same reactions with precisely the same chemical compounds resulting, be they colloids or otherwise. These processes are repeated day after day and year after year as long as life lasts. The process is extremely complicated in such a complex system as the human body, because of the remarkable coordination of different chemical factories required. If for some reason one factory fails to function properly it means that the correct raw material is not furnished to some other factory and disease results. If a portion of body tissue be removed from the body and kept supplied with the food upon which it normally grows, it will probably live many times the length of life of the animal from which it was taken. Such experiments have been performed.

This reasoning may be carried even a step farther. The process of

learning and thinking probably consumes energy; at least a person may feel as fatigued from such work as from manual labor. If this be granted, then we are forced to the conclusion that thinking is a chemical reaction or at least one of the products of a chemical reaction. It remains for the chemists of the future to determine what chemicals are used up and what produced during the processes of memorizing, reasoning, imagining, etc. They will then be able to prescribe what foods to eat or what chemicals to purchase to improve the faculties along any chosen line. This may sound to many as far fetched and simply a flight of the imagination, but some experimental evidence already exists.

This paper will now be concluded by a brief review of some of the work which has been in progress in our own electrochemistry laboratory for several years, the ultimate object of which is to enable us to interpret more intelligently the chemical reactions going on within the human body. After a careful study of what information was at hand concerning the fundamental processes which go on within the body, it became evident that the reactions in which proteins are involved in one manner or another are the most numerous and important. Later developments are confirming this view. It was thought best to start with protein materials which, though not occurring as such in the body, have, nevertheless, the characteristic chemical properties of body proteins and may be obtained in a comparatively pure form. The work thus far has been confined to gelatins. A highly pure ash-free product may be obtained from the Eastman Laboratories. The dependability of this material is illustrated by the fact that samples from two different batches obtained at different times separated by an interval of several years gave identical results. This means that the objection which at one time was legitimate, that work could not be duplicated because different materials give different results, no longer exists.

As I have attempted to show in the earlier part of this paper, every part of the body, even though the body consists almost entirely of colloids, is made up of specific chemical compounds, having absolutely definite composition day after day and year after year. The particular molecules of these compounds that constitute the building stones of the various tissues and fluids of the body are of course continually changing. Some of the atoms of carbon, oxygen, nitrogen, hydrogen, etc., which molecules of these compounds that constitute the building stones of the next year or even tomorrow. The various specific chemical molecules, whether they be in the form of single molecules or associated into colloid aggregates, are continually being decomposed and their places are filled by other molecules of precisely the same chemical composition; these latter must of course be produced through the chemical reactions of the various foods taken into the body. The foods from the time they enter the body until they are transformed into the living tissues, and the tissues

from the time they are formed until they are destroped and finally excreted from the body, are continually in the presence of electrolytic solutions, at one time acid and another neutral and at yet another, alkaline. As stated above, much the most important material and in much the largest amount is protein in some form or another. Probably the simplest and possibly the most general type of chemical action within the body is, then, that between proteins and electrolytes.

As stated previously, gelatin is one of the most common forms of protein material which can be obtained in the pure form. For these various reasons I undertook to make an extensive study, through the application of electrochemical methods, of the nature of the reactions between proteins and electrolytes. So far work has been done with only gelatin. As typical gelatin-acid reactions we have used sulfuric and hydrochloric acids, as typical gelatin-base reactions we have used sodium hydroxide, and as gelatin-neutral salt reactions we have used sodium sulfate and are using silver nitrate. The methods employed have been conductivity, transport numbers by the concentration cell method and also by Hittorf's method, decomposition potentials, concentration cells and the potentials of complex boundaries. As the work has progressed the data have pointed more and more strongly toward a definite chemical reaction between gelatin and electrolytes.

I shall not take time to even outline any of the work except some recently obtained. It is all either now in print or will be soon. This most recent work was obtained through a study of boundary potentials involving gelatin-hydrochloric acid systems. Without going into the details of this work at all, it may be stated that we first studied a system of boundaries between solutions of hydrochloric acid and sodium chloride. The sodium chloride in the solution was obtained by neutralizing part of the hydrochloric acid with sodium hydroxide. The general type of cell system is represented by the following:

Hg sat.	::	0.10 *N*	:	(0.10-x) *N* HCl	:	(0.01-y) *N* HCl	:	0.01 *N*	::	Sat. Hg
HgCl KCl	::	HCl	:	x *N* NaCl	:	y *N* NaCl	:	HCl	::	KCl HgCl
			E_1		E_2		E_3			
Standard Electrode		Solution A		Solution B		Solution C		Solution D		Standard Electrode

The total potentials of the cell is made up of three different diffusion potentials, E_1, E_2, E_3 at the contacts between the solutions A, B, C, D.

A standard calomel electrode was also connected with each of the solutions *B* and *C*. By means of this arrangement it was possible to measure any one of the boundaries, E_1, $E_{,2}$ or E_3 or any combination of them. Several series of determinations were made in which solution *A* was

maintained the same; in solution B, x was changed from 0 to 0.10 N; in solution C, z was changed from 0 to 0.01N; and solution D was maintained constant.

The system above described was then replaced by another of precisely the same type except that, in solutions B and C, x and y represented percents of gelatin. The only distinction between the two systems

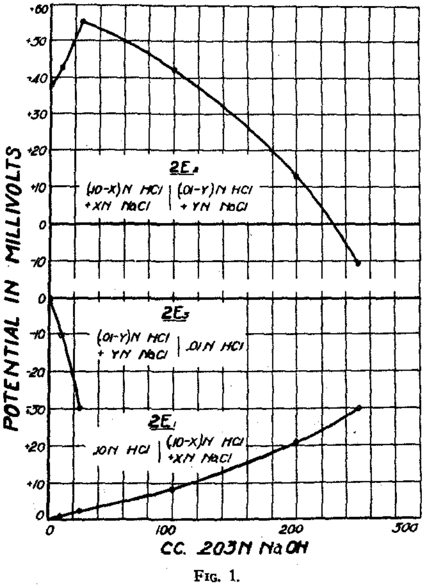


FIG. 1.

was, then, that in one sodium chloride was produced in solutions B and C by the addition of sodium hydroxide to the hydrochloric acid, while in the other something corresponding to the sodium chloride in the first system was formed by the addition of gelatin to the hydrochloric acid in B and C. Through a comparison of the results obtained with these analogous systems, it was hoped to learn something definite about the nature of the reaction between gelatin and hydrochloric acid.

The curves of Figure 1 show the nature of the results obtained with the hydrochloric acid-sodium chloride system. Curve $2E_1$ shows the change in the potential of the boundary represented in the figure as x is increased. The curve, of course, starts at zero since when $x = 0$ the two solutions are identical. The curve ends abruptly when $x = 0.010\ N$

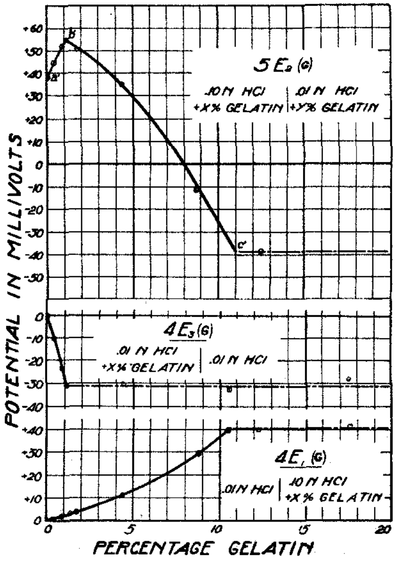


Fig. 2.

or when all of the hydrochloric acid on the right hand side has been neutralized. From this last point it is possible to calculate the combining weight of sodium hydroxide.

Statements corresponding in all respects to those just made for boundary $2E_1$ might be made for boundary E_3.

The curve for boundary E_2 must start at a value corresponding to the potential between pure 0.10 N and pure 0.01 N hydrochloric acid. As sodium hydroxide is added in equal quantities to both sides the con-

centration of acid changes more rapidly on the right hand side, which results, of course, in an increase in boundary potential. After the point is reached, however, at which all the hydrochloric acid on the right side has been neutralized then the potential must decrease to zero and even change direction, since the chloride ion has a greater migration velocity than the sodium ion. The curve must end abruptly when all the acid is neutralized on both sides.

Curve $2E_1$ gives one; curve $2E_3$ another, and curves $2E_2$ give two more independent values from which it would be possible to calculate the combining weight of sodium hydroxide.

Let us now turn our attention to the analogous system in which gelatin was added to the hydrochloric acid solutions in the place of sodium hydroxide. The curves are represented in Figure 2.

Curve $4E_1G$ shows the change in boundary potential which results from the addition of increasing quantities of gelatin to the right hand side of the boundary represented in the figure. The curve should start, of course, at zero, since 0.10 *N* acid exists on both sides. As gelatin is added the values for the potentials change as one would expect if hydrochloric acid were removed from the solution. The curve breaks abruptly as would be expected if the acid were completely removed from the right hand side. Further additions of gelatin produced no appreciable effects.

Statements similar to those just made for boundary $4E_1G$ might be made also for boundary $4C_3G$.

Curves $5E_2G$ are for the boundary represented in the figure. The curve starts at a point corresponding to the boundary potential between 0.10 *N* and 0.01 *N* hydrochloric acid. As equal quantities of gelatin are added to each side, the potential increases, as would be expected if hydrochloric acid were removed in proportion to the amount of gelatin added. As more and more gelatin is added, the curve takes a sudden break which would be expected at the point where all the gelatin is removed from the right hand side. From this point the values gradually decrease to the point where all the acid is removed from the left hand side, and here is found another sharp break, since continued additions of gelatin produce no further changes in potential.

The striking similarity between the corresponding curves in Figures 1 and 2 is clearly evident. The two cell systems from which the data for these two sets of curves were obtained were identical except for the single condition that in one sodium hydroxide was added in increasing quantities to one or to both sides of the boundary, while in the other gelatin was added. The similarity of the corresponding curves in the two sets indicates that the gelatin behaves in the same manner as sodium hydroxide. It was pointed out that in the system where sodium hydroxide was used the four breaks in the curves give four independent sets of data from which could be calculated the combining

weight of sodium hydroxide. If these statements are accepted, then it must be concluded that the four breaks in the curves of figure 2 give four independent sets of data from which to calculate the combining weight of gelatin. All four give identically the same value, 1090, for the combining weight. It should be noted that this shows also that the combining weight is the same for both 0.10 N and 0.01 N hydrochloric acid.

It might be mentioned that curves drawn from values calculated on the basis of Henderson's formula for boundary potential agree well with those given in Figure 1, and also, that by making certain assumptions concerning the concentrations and velocity of the gelatin ions, corresponding values for the gelatin-acid systems were calculated and the agreement between the curves so obtained and those given in Figure 2 is good. The boundaries here studied are similar in type to some with which J. Loeb worked, but the close agreement between the experimental curves for the gelatin-acid systems and those calculated on the basis of Henderson's diffusion formula indicates that the potentials are due to ordinary diffusion rather than the Donnan equilibrium as Loeb assumed.

The work is to be continued with other acids, with bases, and with salts; also similar whole systems will be worked out for other proteins. A complete presentation of the work briefly outlined in the latter part of this paper will appear as a series of articles in the Journal of the American Chemical Society.

Note

During the last few years there have appeared several articles describing the great therapeutic value of several medicinal substances in the colloidal form. This is the only form in which free elements may be administered, in most cases at least, and it appears that the free elements are highly effective. It is stated that iodine and mercury, as ordinarily used, are unsatisfactory because of their toxic action, but in the colloidal form they are free from this difficulty. Silver and iodine do not stain the skin when in the correct colloidal form. It is claimed that intravenous injections of colloidal preparations are painless.

One difficulty has been to get medicinals through the stomach without having them changed there; this is particularly true of iron. It is claimed that in the colloidal form this difficulty has been overcome.

Other elements which have been prepared and used with good success are: antimony, manganese, copper, platinum, palladium, nickel, sulfur, arsenic, and several of the alkaloids.

From the remarkable success attending the very small amount of work which has been done thus far in the preparation of medicinals in the colloidal form, it would seem that there are wonderful opportunities here for work in chemotherapy.

University of Michigan,
Ann Arbor, Michigan.

PHYSICO-CHEMICAL STUDIES ON PROTEINS

III. PROTEINS AND THE LYOTROPIC SERIES[1]

BY ROSS AIKEN GORTNER, WALTER F. HOFFMAN AND WALTON B. SINCLAIR

Hofmeister[2] was apparently the first to investigate on an extensive scale the effect of different salts upon the physical properties of proteins. The initial paper from his laboratory[3] was followed by others[4] and as a result of his experiments he drew the conclusion that when salts of the same cation were used the anions could be arranged in a series corresponding to the effect which the salts produced upon the physical properties of protein-water systems. He also observed that a similar series could be formed by noting effects produced by varying the cations but using salts with a common anion.

These series representing ion effects are especially noted in such phenomena as viscosity of protein sols, the swelling of gelatin or other proteins in aqueous media or the reverse, the precipitation of proteins from an aqueous sol.[5]

The arrangement of the anions most commonly found is citrate > tartarate > SO_4 > acetate > Cl > NO_3 > Br > I > CNS where citrate shows the greatest precipitating effect and thiocyanate the least. The cation effects are in general less marked, if we except those cations which form irreversible precipitates with proteins, but may be expressed approximately as K > RB > Na > Cs > Li > NH_4.

These or similar series of ionic effects have come to be known as the lyotropic series or the Hofmeister series of ions. Various theories have been propounded to account for the observed actions of the different salts. Thus Jaeger[6] finds that the surface tension of the molten alkali salts at 1000° C. shows a series of F > SO_4 > Cl > Br > NO_3

[1] Contribution from the Division of Agricultural Biochemistry, University of Minnesota. Published with the approval of the Director as Paper No. 707, Journal Series, Minnesota Agricultural Experiment Station.

[2] Hofmeister, F., "Zur Lehre von der Wirkung der Salze. Zweite Mittheilung." *Arch. exp. Path. u. Pharm.*, 24, 247-60 (1888).

[3] Lewith, S., "Zur Lehre von der Wirkung der Salze. Erste Mittheilung," *Arch. exp. Path. u. Pharm.*, 24, 1-16 (1888).

[4] Hofmeister, F., "Zur Lehre von der Wirkung der Salze. Dritte Mittheilung, Fünfte Mittheilung. und Sechste Mittheilung." *Arch. exp. Path. u. Pharm.*, 25, 1-30 (1889); 27, 395-418 (1890); 28, 210-238 (1891).

[5] Pauli, W., "Untersuchungen über physikalische Zustandsänderungen der Kolloide. II Verhalten der Eiweisskörper gegen Elektrolyte." *Beitr. Chem. Physiol. u. Pathol.*, 3, 225-46 (1902).

[6] Jaeger, F. M., "Temperatur abhängigkeit der molekuloren freien Oberfläschenenergie von Flüssigkeiten im Temperaturbereich von — 80 bis + 1650° C." *Z. anorg. u. allgem. Chem.*, 101, 1 (1917).

> I and Li > Na > K > Rb > Cs. Essentially the same order holds for the effect of these ions in increasing the surface tension of water. There is a pronounced increase in surface tension in fluoride and sulfate solutions but little if any increase in the surface tension of iodide- and sulfocyanate-containing solutions. Freundlich [7] suggests that "in all probability this series also corresponds to the order of the hydration of the ions . . . the most hydrated ions are at the sulfate and lithium ends of the lyotropic series." Remy [8] has calculated the hydration of certain ions, on the assumption that an ion is a sphere and that if it moves in a viscous medium it should obey Stokes' law. Accordingly from a study of ionic mobility he finds the degree of hydration as indicated in Table 1.

TABLE 1.—THE DEGREE OF HYDRATION OF SOME OF THE COMMON IONS.[1]

Ion	H^+	Cs^+	Rb^+	K^+	NH_4^+	Na^+	Li^+	Ag^+	
Molecules of water of hydration	0	13	14	16	17	<66	<120	29	
Ion	Pb^{++}	Ba^{++}	Sr^{++}	Ca^{++}	Mg^{++}	Cu^{++}			
Molecules of water of hydration	20	27	35	35	52	48			
Ion	OH^-	I^-	Br^-	Cl^-	ClO_4^-	ClO_3^-	NO_3^-	CNS^-	$SO_4^=$
Molecules of water of hydration	1	15	14	16	17	26	19	25	14

[1] Remy, *Z. physik. Chem.*, 89, 467 (1915).

Frumkin [9] has devised a technic for measuring the potential difference which exists between the surface of a liquid and the air above it. He points out that this affords a means of measuring the nature of the surface film in solutions and explains his results on the assumption that adsorption in the surface layer is related to the affinity of a particular anion or cation for water. A part of his data is shown in Table 2.

He constructs a lyotropic series showing the effect of the anion on the phase boundary potential, the anions ranging themselves in the order F, $SO_4 < Cl < Br < NO_3 < I < CNS$, and states [10] "Die negative Aufladung ist umso stärker, je weniger hydrophil das Anion ist. Ist die Verwandtschaft des Anions zum Wasser gross, so dringst das Salz in die Oberflächenschicht nicht ein und die P.D. Luft/Lösung ist mit der P.D. Luft/Wasser identisch; ist sie dagegen klein, so tritt eine merkliche Anionenadsorption auf und die Oberfläche wird negativ aufgeladen."

[7] Freundlich, H., "Colloid and Capillary Chemistry." E. P. Dutton and Co., N. Y., 1926, p. 58.

[8] Remy, H., "Beiträge zum Hydratproblem I. Berechnung der Menge des die Ionen einhüllenden Wassers aus den Elektrolytischen Beweglichkeiten." *Z. physik. Chem.*, 89, 467-88 (1915).

[9] Frumkin, A., "Potentialdifferenzen zwischen Flüssigkeiten und Luft." *Kolloid-Z.*, 35, 340-2 (1924).

[10] *Ibid.*, p. 340.

TABLE 2.—THE PHASE BOUNDARY POTENTIALS, ε, BETWEEN AIR AND THE SURFACE LAYER OF CERTAIN INORGANIC SALT SOLUTIONS.[1]

Electrolyte	Solution $N/1$ ε(Millivolts)	Solution $2N$ ε(Millivolts)
KF	....	+ 5
KCl	− 2	− 6
KBr	−10	−16
KI	−34	−52
KCNS	−57	−87
KOH	0	+ 5
K_2CrO_4	....	− 1
K_2CO_3	....	+ 3
NaI	−39	−55
$NaNO_3$	−17	−23
NaCl	− 1	− 4
Na_2SO_4	+ 3	....
Na_2CO_3	+ 3	+ 5
RbCl	....	− 7
CsCl	....	− 6
LiCl	....	− 9.5
$Al_2(SO_4)_3$	0	+ 6
HF	−71	−103
HCl	−23	−55
HBr	−34	−78
HI	−61	−112
H_2SO_4	−13.5	−55 (?)
H_3PO_4	− 0.5	....

[1] Frumkin, "Phasengrenzkräfte und Adsorption an der Trennungsfläsche Luft/Lösung anorganischer Elektrolyte," *Z. physik. Chem.*, **109**, 34 (1924).

Freundlich and Aschenbrenner [11] also agree that the position of the fluorine ion in the lyotropic series is probably associated with a high degree of hydration and cites as confirmatory evidence the heat of hydration as measured by Fajans,[12] i.e., $F^- = 129$, $Cl^- = 88$, $Br^- = 79$, and $I^- = 68$ kilogram calories per gram ion.

This view that F^- and SO_4^{--} are more highly hydrated than, for example, CNS^-, is directly opposed to the data of Remy as shown in Table 1, and it appears probable to us that in addition to the hydration of the ions we must also consider the orientation of the salt molecules in the surface film, and the orientation of the water molecules surrounding the ions of the salt. This question as to the orientation of water molecules on surfaces as affecting colloidal behavior has been discussed at considerable length in a separate paper.[13] Thus Frumkin's data would indicate that in KF solution the cation tends to be oriented toward the air portion of an air-water interface, whereas a progressively increasing orientation of the anion toward the surface occurs as we pass from KCl to KCNS. On this theory the action of KF on an aqueous colloid system would be determined more by the cation than by the anion, whereas for solutions of KCl, KBr, KI and KCNS the effect of the anion would progressively overshadow that of the cation.

In a later paper Frumkin [14] shows that the potential differences which he observed in the series $F < Cl < Br < NO_3 < I$ were reflected in the

[11] Freundlich, H. and Aschenbrenner, M., "Ueber die lyotropen Eigenschaften des Fluorions." *Kolloid-Z.*, **41** 35-40 (1927).
[12] Fajans, von K., "Löslichkeit und Ionisation vom Standpunkte der Atomstruktur." *Naturwissenschaften*, **9**, 729-38 (1921).
[13] Gortner, R. A., "Adsorption and Vital Phenomena." A Lecture delivered at Washington University, St. Louis; the University of Iowa; the Des Moines Academy of Medicine; the Mayo Clinic, Rochester Minnesota; and the University of Minnesota, in the spring of 1926, in a Series of Lectures on "Colloids in Biology" under the Auspices of the Mayo Foundation. (These lectures will shortly appear in book form.)
[14] Frumkin, A., "Ueber Ionenadsorption an der Wasseroberfläsche." *Kolloid-Z.*, **40**, 9-11 (1926).

effect of these ions on the surface tension of aqueous solutions. Using the corresponding acid salts of tetrapropyl ammonium hydroxide, he observed in 0.5 *N* solutions, surface tension depressions, expressed in dynes per sq. cm. as differences from the surface tension of pure water, of $F^- = 7.48$, $Cl^- = 8.30$, $Br^- = 9.33$, $NO_3^- = 10.09$ and $I^- = 16.36$.

That the salts of fluorine do show a special behavior toward colloid systems is further evidenced by the work of Freundlich and Aschenbrenner,[14] where, studying the lyotropic behavior of the fluorine ion, they find that in comparison with Cl^-, Br^-, I^- or CNS^- it (1) shows the greatest lowering of the solubility of phenyl-thiourea, (2) increases the "setting point" of a gelatin sol, whereas the other salts lower the "setting point," (3) increases markedly more than the other salts the viscosity of a gelatin sol, and (4) is unusually efficient in promoting the coagulation of positively charged suspensoid sols (Fe_2O_3 and CuO), approaching in this respect the efficiency of divalent anions.

Harned[15] has determined the ionic concentration product of water in NaCl, KCl, NaBr, and KBr solutions of various concentrations. He finds that in each series the molal concentration of dissociated water molecules per 1000 grams of water (M_w) is appreciably greater for sodium salts than for potassium salts of equivalent concentration and that the bromide solutions are furthermore characterized by a greater value for M_w than are the corresponding chloride solutions. The water dissociation reaches a maximum value in about 0.5 molar solutions and then decreases so that in strong solutions ($> 1.5\ M$) it may be less than in pure water. Unfortunately data of this sort are altogether too few to enable us to draw any general conclusions as to the rôle which water dissociation may play in the phenomena of the lyotropic series. Possibly the effect that Harned observed is due to the hydration of the ions of the salt removing undissociated water molecules from the sphere of action so that there is an apparent increase in the H^+ and OH^- as related to the concentration of the uncombined water molecules.

Bayliss[16] and McBain[17] suggest that the lyotropic series may be due to the intensity of adsorption of the ions concerned. Bancroft[18] apparently agrees with the differential adsorption theory, but recently[19] he has proposed another theory that the effect may be produced by a displacement of the water equilibrium from a polyhydrol form $(H_2O)_n$ to hydrol (H_2O) or *vice versa*. He notes that there is no experimental

[15] Harned, H. S., "The Activity Coefficient and Ionic Concentration Product of Water in Sodium and Potassium Chloride Solutions," *J. Am. Chem. Soc.*, 47, 930-40 (1925); "The Dissociation of Water in Potassium and Sodium Bromide Solutions," *J. Phys. Chem.*, 30, 1060-72 (1926).

[16] Bayliss, W. M., "Colloid Chemistry in Physiology." Second Report on Colloid Chemistry and its General and Industrial Applications. London, 1918, pp. 117-54.

[17] McBain, J. W., "A Survey of the Main Principles of Colloid Science." Colloid Symposium Monograph, vol. 4, 1926, pp. 7-18.

[18] Bancroft, W. D., "Applied Colloid Chemistry." McGraw-Hill Book Co., N. Y., 1921, p. 253.

[19] Bancroft, W. D., "The Water Equilibrium," "Colloid Symposium Monograph" vol. 4, 1926, pp. 29-37.

evidence to show in which direction the equilibrium $(H_2O)_n \leftrightarrows H_2O$ is shifted by any particular salt. This hypothesis should open a new field in physico-chemical research, because if such a shift in the water equilibrium is produced, and, combining this with the suggested possible explanation of Harned's observations,[18] it would appear that the dissociation of water may occur according to the following scheme:

$$(H_2O)_n \rightleftarrows (H_2O)_3 \rightleftarrows (H_2O)_2 \rightleftarrows H_2O \rightleftarrows H^+ OH^-$$

in which case the amount of change in the concentration of H_2O may not be a negligible factor when we calculate K_w.

In view of the almost unanimity of opinion of investigators regarding the existence of a lyotropic series it is somewhat surprising to note that Loeb denies the existence of a lyotropic series, at least in so far as protein behavior is concerned. He states [19a] "The Hofmeister series of ions are the result of an error due to the failure to notice the influence of the addition of a salt upon the hydrogen-ion concentration of the protein solution. As a consequence of this failure, effects caused by a variation in the hydrogen-ion concentration of the solution were erroneously attributed to differences in the nature of the ions of the salts used," and [20] "As long as these Hofmeister ion series were believed to have a real existence it seemed futile to decide for or against a purely chemical theory of the behavior of colloids since even with a bias in favor of a chemical theory the Hofmeister series remained a riddle.

"The writer believes that he has removed these difficulties by using protein solutions of equal hydrogen-ion concentration as the standard of comparison.

"In this way it was found that a number of authors had erroneously attributed the effects of an alteration of the hydrogen-ion concentration upon the physical properties of a protein to a difference in the specific action of the anion or cation added. Thus it was always believed that acetates have almost as great a 'dehydrating' action as sulfates, but it was overlooked that acetic acid is a weak acid, and that in the experiments referred to the authors failed to compare the effects of SO_4 and CH_3COO at the same hydrogen-ion concentration. When this error is avoided it can be shown that acetates influence the swelling, osmotic pressure, and viscosity of protein solutions in the same way as chlorides or nitrates, but not in the same way as sulfate; in other words, anions of the same valency act alike.

"By taking into consideration the hydrogen-ion concentration it was possible to show that the assumption of specific differences in the

[19a] Loeb, J., "Ion Series and the Physical Properties of Proteins. III The Action of Salts in Low Concentrations," *J. Gen. Physiol.*, 3, 391-414 (1920-21). Quotations from p. 414.

[20] Loeb, J., "Proteins and the Theory of Colloidal Behavior." McGraw-Hill Book Co., N. Y., 1922, pp. 14-15.

action of different ions of the same valency and sign of charge was due to a methodical error; and that the Hofmeister rule must be replaced by a simple valency rule, according to which only the valency and sign of charge of an ion influence the colloidal behavior of a protein but that the other properties of the ion have no influence as long as no constitutional change in the protein molecule occurs."

Bancroft[21] has already pointed out certain objections to the line of reasoning adopted by Loeb, and McBain[17] remarks "The effects of the Hofmeister or lyotrope (Freundlich) series of ions is too striking to be ignored. They have been observed with too many types of colloids and in connection with too many systems not even containing colloids to be attributed to systematic experimental error."

It is the purpose of the present paper to present certain evidence based, as were the experiments of Loeb, upon protein properties. We believe that these observations constitute one of the most striking demonstrations of the existence of a lyotropic series as affecting protein systems.

Hoffman and Gortner,[22] in an attempt to isolate a quantity of the various proteins which have been reported to occur in wheat flour observed that the extraction of the flour with 5 percent potassium sulfate solution and 10 percent sodium chloride solution did not yield similar protein fractions. Marked differences were observed in the amount and character of the protein material dissolved by these solutions and in the amount of protein which could be separated from these solutions. These differences were especially noticeable in the "globulin" fraction.

The class of proteins known as globulins has been defined by the Physiological and Biochemical Committees on Protein Nomenclature[23] as "simple proteins insoluble in pure water but soluble in neutral solutions of salts of strong bases with strong acids. (The precipitation limits with ammonium sulfate should not be made a basis for distinguishing the albumens from the globulins.)" This definition is indefinite in that no statement as to the concentration of the salt solution is given. In the majority of textbooks on physiological chemistry this omission is in part remedied in that the definition is worded more or less similarly to the definition of Mathews[24] "Globulins.—Simple proteins, heat coagulable, insoluble in water but soluble in dilute solutions of salts of strong acids and bases." In so far as our search of the literature has extended no one appears to have definitely raised the question of *what salts* and *what*

[21] "Applied Colloid Chemistry," p. 256.

[22] Hoffman, W. F. and Gortner, R. A., "The Preparation and Analysis of the Various Proteins of Wheat Flour with Especial Reference to the Globulin, Albumen and Proteose Fractions." *Cereal Chem.*, 4, 221-29 (1927).

[23] Joint Recommendations. *J. Biol. Chem.*, 4, xlviii-li (1908); *Amer J. Physiol.*, 21, xxvii-xxx (1908).

[24] Mathews, A. P., "Physiological Chemistry." William Wood and Co., N. Y., 1915.

concentrations. It is in part the purpose of this study to raise these questions and to point out that if our experimental results are valid the definition of globulin as universally used at the present time is wholly meaningless.

Experimental Work

The Material.—The material which we have chosen for this study consisted of twelve samples of wheat flour and included flours milled from most of the important commercial types of wheat. The wheats from which these flours were milled were likewise grown under widely different climatic and geographical environments. Grewe and Bailey [25] have recorded the origin, type and grade of these flour samples and have reported certain observations in regard to the physical and chemical properties of these flours as related to the problems of the cereal chemist. It is not the purpose of this communication to discuss our experimental data on these flours in their relation to cereal chemistry problems. A preliminary report of some of these applications has already been made by Gortner[26] and an extended discussion of the data will be presented elsewhere by the present authors.

Inasmuch as the present communication is intended to deal only with the general colloid problem we will consider the flour used only as a source of biological material in which five classes of protein, i.e., albumin, globulin, prolamine, glutelin and proteose, have been considered to be invariably present.

The salts used were of the highest purity obtainable commercially. All the solutions were made up by weighing out the salts from freshly opened original containers.

The Method.—Six grams of wheat flour was suspended in 50 cc. of a salt solution of known concentration and the suspension shaken for 30 minutes in a mechanical shaker. The flour residue was then tightly packed in the bottom of the tube by whirling in an electric centrifuge, centrifuging being continued until the supernatant liquid was clear. The supernatant liquid was then carefully decanted into a Kjeldahl flask and a second extraction of the flour residue was carried out by adding a fresh 50 cc. portion of the salt solution, shaking for 30 minutes, centrifuging and decanting into the same Kjeldahl flask. A third extraction was similarly made. The protein dissolved by the three successive salt extractions was then determined on the combined extracts by the usual Kjeldhal-Gunning procedure. Nitrogen and moisture were determined on the flour samples and the salt extraction data calculated on

[25] Grewe, E. and Bailey, C. H., "The Concentration of Glutenin and other Proteins in Various Types of Wheat Flour." *Cereal Chem.*, **4**, 230-47 (1927).
[26] Gortner, R. A., "Correlation of Loaf Volume with Peptizing Action of Salts on Wheat Flour Protein," *Proc. Soc. Exper. Biol. Med.*, **24**, 530-2 (1927).

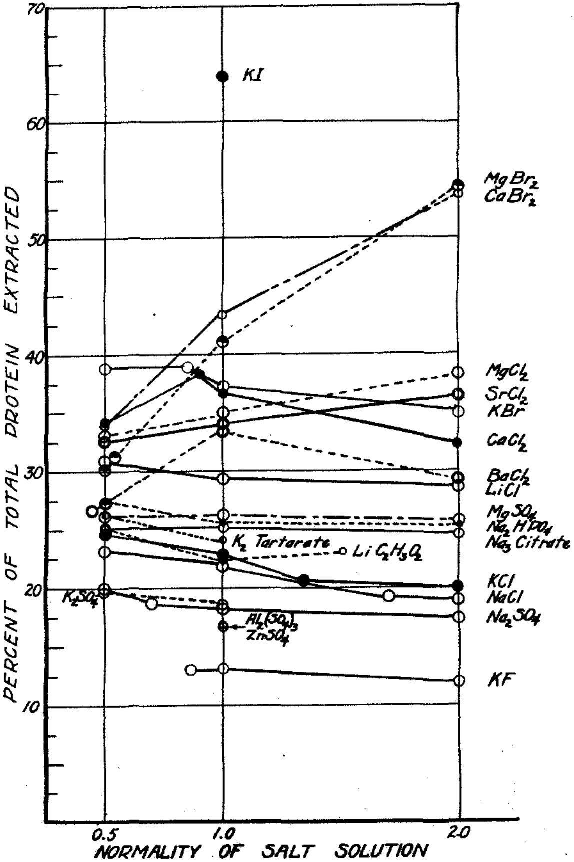


FIG. 1.—The average percentage of protein extracted from (12) wheat flours by various concentrations of salt solutions.

the moisture free basis as percent of total protein dissolved (i.e., peptized) by the salt solution. Duplicate extractions were made in all instances, and in case the usual limit of error for a Kjeldahl determination was exceeded in the percentage of nitrogen extracted, the extractions were repeated on additional samples until satisfactory analytical agreement was obtained.

The *average* per cents of protein peptized by the different salts in their different concentrations are shown in Table 1 and graphically in Figure 1. The values shown in Table 1 are the average values of at

TABLE 1.—AVERAGE PERCENTAGE OF TOTAL PROTEIN [1] EXTRACTED FROM (12) WHEAT FLOURS BY VARIOUS CONCENTRATIONS OF SALT SOLUTIONS.

	Concentration of Salt Solution		
Salt	0.5 *N*	1.0 *N*	2.0 *N*
Li Acetate	25.01	22.32	....
LiCl	30.08	29.32	28.60
NaCl	23.16	21.68	18.97
Na_2SO_4	20.00	18.20	17.30
Na_3 Citrate	25.07	25.13	24.52
Na_2HPO_4[2]	27.44	25.62	25.32
KF	....	13.07	11.93
KCl	24.62	22.77	20.01
KBr	38.77	37.22	34.91
KI	....	63.89	....
K_2SO_4	19.68	18.59	....
K_2 Tartrate	26.35	24.12	....
$KCrO_4$	26.92	....	....
$MgCl_2$	33.01	34.99	38.35
$MgBr_2$	30.17	40.11	54.38
$MgSO_4$	26.18	26.35	25.69
$CaCl_2$	34.14	36.60	32.25
$CaBr_2$	33.90	43.27	53.68
$SrCl_2$	32.59	34.50	36.47
$BaCl_2$	27.29	33.42	29.24
$ZnSO_4$	....	16.71	....
$Al_2(SO_4)_3$	....	16.90	....

[1] Each figure represents the average of at least 24 separate nitrogen determinations.
[2] Considered as a *divalent* salt.

least 24 individual nitrogen determinations and accordingly must be regarded as having a very small probable error. Figure 1, in addition to recording the values shown in Table 1 includes part of another series of determinations where 5 or 10 percent concentrations of salt solutions were used. For the purpose of the graph these concentrations were converted into normalities and the positions of the points shown on the curves.

Table 2 shows the hydrogen-ion concentration (as pH, determined electrometrically) of certain of the salt solutions and of the salt solution extracts of two of the wheat flours. These flours differed greatly in the ease with which their proteins were peptized by the salt solutions. At

TABLE 2.—THE HYDROGEN-ION CONCENTRATION OF THE EXTRACTS FROM FLOURS NO. 1 AND NO. 4.

1.0 *N* Salt Solution	pH Salt Solution	pH Salt Solution Extract of Flour No. 1	pH Salt Solution Extract of Flour No. 4	Per Cent of Total Protein Extracted from Flour 1	4
NaCl	6.49	5.80	5.65	25.4	19.2
Na_3 Citrate	8.03	7.56	7.40	42.5	15.6
Na_2HPO_4	9.13	8.74	8.66	41.5	16.6
Na_2SO_4	6.44	5.80	5.63	25.7	14.8
KCl	8.67	6.05	5.87	30.4	18.7
KBr	6.33	6.00	5.87	48.6	30.1
K_2SO_4	6.94	5.93	5.77	26.2	14.8
K_2 Tartrate	7.46	6.80	6.59	34.6	18.4
$MgCl_2$	5.48	5.24	5.06	47.0	29.1
$MgSO_4$	7.74	5.85	5.70	41.6	19.6
$CaCl_2$	5.55	4.92	4.87	47.2	30.9
$SrCl_2$	6.37	5.29	5.21	44.4	29.1
$Al_2(SO_4)_3$	2.90 [3]	...	...	23.0	14.2
Aqueous Extract of Flour	...	5.83 [1]	5.57 [2]	...	...

[1] Data from Grewe and Bailey (*ref. cit.*). This flour requires 1.3 cc. of 0.1 *N* lactic acid to bring an aqueous suspension containing 10 grams of flour to a pH of 5.00.
[2] Data from Grewe and Bailey (*ref. cit.*). This flour requires 1.0 cc. of 0.1 *N* lactic acid to bring an aqueous suspension containing 10 grams of flour to a pH of 5.00.
[3] Through an error the pH of the extracts of Flours 1 and 4 were not determined. The extract of Flour No. 2 had a pH of 2.90, showing that the flour did not buffer the aluminum sulfate solution. Aluminum sulfate extracted 14.7% of the total protein from Flour No. 2.

the time the experiments were made it was not thought worth while to determine the hydrogen-ion concentration on all of the salt solutions and the flour extracts. The data in Table 2 can be regarded as showing the extreme ranges, as well as demonstrating that most of the extracts showed pH values of approximately 5.0-6.0, which is essentially the hydrogen-ion concentration of distilled water in equilibrium with the carbon dioxide of laboratory air.

DISCUSSION

The Lyotropic Series.—The data of Table 1 and Figure 1 present very striking evidence of a lyotropic series as affecting protein peptization. The figures for the percent of protein peptized by the potassium halides are outstanding in this respect and arrange themselves in the order KF < KCl < KBr < KI. In this particular series there can be no question of an influence of hydrogen-ion concentration for all of these solutions and extracts were essentially identical in pH values.

Considering those salts which have potassium as the cation we find for *N*/2 concentrations a series F < SO_4 < Cl < tartarate < CrO_4 < Br; for *N*/1 concentrations F < SO_4 < Cl < tartarate < Br < I; and for 2*N* concentrations F < Cl < Br. The same relative order holds for all the concentrations of the salts studied.

Taking now the salts where chlorine is the anion, we find in *N*/2 solutions a series Na < K < Ba < Li < Sr < Mg < Ca; for *N*/1 solutions Na < K < Li < Ba < Sr < Mg < Ca; and for 2*N* solutions Na < K < Li < Ba < Ca < Sr < Mg. Only two changes are noted in these three series. In passing from *N*/2 to *N*/1 solutions barium and lithium exchange places, and in passing from the *N*/1 to the 2*N* series calcium is placed lower than strontium and magnesium. In general, however, the order is relatively constant with the alkali chlorides showing lower peptizing effects than do the chlorides of the alkaline earths.

The behavior of the halogen salts with increasing concentration is interesting. Thus KF, KCl, KBr, NaCl, and LiCl all show *decreasing* peptizing properties with increasing concentration of salt. Calcium chloride and barium chloride show a slight increase in peptizing power in *N*/1 concentrations hut a decrease in 2*N* concentrations, whereas $MgCl_2$, $MgBr_2$, $SrCl_2$, and $CaBr_2$ produce *increasing* peptization with increased concentration, this increase being very marked in the case of the $MgBr_2$ and $CaBr_2$ solutions. Unfortunately the iodides of the alkaline earths undergo too great hydrolysis in aqueous solution to be utilizable in a study such as this, and furthermore, we were unable to secure samples of barium bromide and strontium bromide for comparison with the other salts. It is not believed, however, that they would have differed markedly from the magnesium and calcium hromides.

The Influence of Hydrogen-Ion Concentration.—Table 2 shows the hydrogen-ion concentration of certain of the salt solutions which were used in this study together with the hydrogen-ion concentration of the extracts from Flours No. 1 and 4 as well as the percent of total protein extracted from these flours. These flours were selected because the proteins of Flour No. 1 were almost invariably the most easily peptized, while Flour No. 4 almost always showed the lowest percentage of protein peptization.

The majority of the salts used gave essentially neutral solutions. Since wheat flours are themselves fairly efficient buffer systems,[27] the citrates, phosphates and tartarates were purposely included so as to provide highly buffered and somewhat alkaline solutions. Similarly aluminum sulfate was employed so as to give a rather constant acidic solution. No explanation is available for the high pH of the KCl solution but it will be noted that only an insignificant trace of alkali could have been present for when this solution was added to the flours it reacted almost immediately with the buffers in the flour and approximated the pH of the NaCl and NaBr solutions.

It is perfectly obvious from an inspection of Tables 1 and 2 and

[27] Bailey, C. H. and Peterson. A. C., "Studies on Wheat Flour Grades. II Buffer Action of Water Extracts." *J. Ind. Eng. Chem.*, 13, 916-8 (1921).

Figure 1 that hydrogen-ion concentration is not playing a major rôle in the peptizing action of the salts. Thus for example the flour extracts where KF, KCl, KBr, and KI solutions were employed, differed only insignificantly in pH values but the amount of protein peptized was very striking. However it was thought worth while to analyze the data by statistical methods. Accordingly we have computed the correlation coefficient (r) as related to pH and per cent of total protein peptized. Five correlations have been made using the formula proposed by Harris.[28]

1. The correlation between pH of the salt solution extract of flour No. 1 and the per cent of protein peptized [columns 3 and 5 of Table 2, omitting $Al_2(SO_4)_3$] was found to be $r = -0.023 \pm 0.195$.

2. The similar correlation for flour No. 4 [columns 4 and 6 of Table 2, omitting $Al_2(SO_4)_3$] was found to be $r = -0.559 \pm 0.140$.

3. The correlation combining flours Nos. 1 and 4 but leaving out the $Al_2(SO_4)_3$ extracts gave (n = 24) $r = -0.112 \pm 0.136$.

4. The correlation between the initial pH of the salt solution and the average per cent of protein extracted from all the flours [column 2 of Table 2 and column 4 of Table 1 including the $Al_2(SO_4)_3$ series] was -0.030 ± 0.187.

5. The correlation obtained as under (4) but omitting the $Al_2(SO_4)_3$ series was -0.416 ± 0.161.

Three of the above values show that there is no relationship between the pH of the salt solution and the percentage of protein which is peptized. Two of the values indicated a slight negative relationship. In one instance r is four times its probable error, but in the other instance it is less than three times its probable error, so that in any event the relationship is very slight. The negative sign of r would indicate that the lower the pH the greater would be the peptizing effect. We believe this to be a concomitant phenomenon and not a causal relationship and to be due to the fact that certain salts which have a high peptizing value (salts of divalent cations) are also characterized by being somewhat hydrolyzed in aqueous solutions. This belief is confirmed when we consider that the aluminum sulfate solution, although it has the highest hydrogen-ion concentration of all the salts tested, had likewise nearly the lowest peptizing value, and that when it is included in the correlation formula it reduces a correlation of $r = -0.416 \pm 0.161$ to $r = -0.030 \pm 0.187$, whereas if there were a real relationship between the pH of the salt solution and peptizing properties, the correlation should have been increased rather than reduced.

An inspection of the data of Table 2 supports the view that the correlation, $r = -0.559 + 0.140$, does not indicate a causal relationship. When the data for Flours Nos. 1 and 4 are compared, it will be noted

[28] Harris, J. A., "The Arithmetic of the Product Moment Method of Calculating the Coefficient of Correlation." *Amer. Nat.*, 44, 693-99 (1910).

that the variation of per cent of protein extracted, from the mean per cent of protein extracted ($\bar{\Sigma}$) is greater for Flour No. 1 than for Flour No. 4 [Flour No. 1, omitting $Al_2(SO_4)_3$, $\bar{\Sigma} = 37.09$ per cent protein with extreme variations from the mean of $+ 11.51$ per cent and $- 11.69$ per cent; Flour No. 4, omitting $Al_2(SO_4)_3$, $\bar{\Sigma} = 21.41$ per cent with extreme variations of $+ 8.69$ per cent to $- 6.61$ per cent], whereas the reverse is true for the variations in pH [Flour No. 1, omitting $Al_2(SO_4)_3$, $\bar{\Sigma}$ pH $= 6.16$ with extreme variations from the mean of $+ 2.58$ pH to $- 0.92$ pH; Flour No. 4, omitting $Al_2(SO_4)_3$, $\bar{\Sigma}$ pH $= 6.02$ with extreme variations from the mean of $+ 2.64$ pH to $- 1.17$ pH].

Thus, Flour No. 4, which shows the apparently significant correlation, yields extracts showing the *greatest* variability in *pH* but the *least* variability in per cent protein extracted, whereas if hydrogen ion concentration were the causal factor, the flour showing the greatest range in pH should likewise have shown the greatest range in protein extracted.

Additional proof that hydrogen-ion concentration is not playing a major rôle is afforded by the KF $<$ KBr $<$ KCl $<$ KI series, where, as already noted, the salts are not characterized by being hydrolyzed in aqueous solution and where the hydrogen-ion concentration of the extract is determined by the buffering effect of the wheat flour. *Here we have a range in per cent of total protein extracted of from* 13.07 *per cent to* 63.89 *per cent which can be due only to an influence of the specific anions, all being present in equivalent concentration.*

Another indication that hydrogen-ion concentration is relatively unimportant is afforded by a comparison of the curves for disodium phosphate, sodium citrate and magnesium sulfate solutions. Here we have a neutral salt, the extract having a pH of 5.70-5.85 and two highly buffered somewhat alkaline solutions ranging in pH values from pH 7.40 to pH 8.66, nevertheless the per cent of protein extracted by the three salts is almost identical.

Accordingly we must conclude that Loeb was in error in stressing the hydrogen-ion concentration differences as being largely if not entirely responsible for the Hofmeister series effects and we must insist that *there is a lyotropic series of ionic effects in an aqueous system of protein and salts, and that these effects are due to properties of the anion and the cation of the salt and are observable and measurable even at a constant hydrogen-ion concentration.* In fact the specific properties of certain anions or cations may be so great as to entirely overshadow relatively large changes in hydrogen-ion concentration.

What is a Globulin?—This question would appear to be pertinent in view of the data in Table 1 taken in conjunction with the generally accepted definition of a globulin. It must be obvious to anyone that a definition which is based upon "solubility" (i.e., peptization) in a dilute

salt solution, is, in the light of present results, so ambiguous as to be absolutely meaningless.

It has been generally assumed that the salt peptized fraction of wheat flour protein contains proteins belonging to three different classes, i.e., an albumin, a proteose and a globulin, and that these different classes can be separated from each other by appropriate procedure. Assuming that fractions corresponding in physical properties to an albumen and a proteose could be separated from the salt peptized protein sol, *we do not believe that the residual protein from any one of the various extracts would constitute a chemical entity which should be dignified by the term "globulin."*

It is intended at this point to definitely raise the question as to the justification for the establishment of a system of protein classification based to a considerable extent upon solubility, or better, peptization behavior. Our experiments [22] would indicate that all of the various protein fractions (with the exception of the proteose) which have been considered fixed entities, and characteristic of wheat flours are, if we follow the prescribed routine procedure for protein isolation, capable of realization, but that, if the routine procedure is somewhat altered, fractions having different properties and characteristics are obtained. Thus for example a normal solution of KBr extracts a given percentage of protein from a wheat flour which is far in excess of the amount of protein extracted by a normal solution of KCl. If now the KBr-protein solution is subjected to dialysis, so as to remove the salt, a precipitate of protein is formed as one would expect in dealing with a solution of a "globulin" and *this precipitate is now completely soluble in normal KCl solution.* In the flour, part of the protein was not extractable by KCl solutions, but following a KBr extraction it is peptizable by KCl. Unfortunately far too little is known regarding the factors involved in the peptization of a protein to enable us to assign a cause to these observed facts. The cause is probably complex and will be found to involve the nature of amino acid linkages, secondary valences and polar groups as well as degree of hydration and specific ionic effects.

The term "globulin" has been assigned to a group of proteins separable from the other protein fractions of tissues by a purely arbitrary procedure. The globulins have been separated into euglobulins and pseudo globulins on an equally arbitrary basis. When a globulin is transformed into a protein, e.g., edestin → edestan, it is considered correct to say that the final product shall be classed as a "derived protein" although nothing is known of the nature of the chemical change which has taken place and although the "protean" has, in so far as solubility is concerned, all the characteristics of a "glutelin." No one can say that the "glutelins" occurring in nature are not formed by a "globulin" → "protean" transformation. A great many fixed ideas and traditions as related to protein chemistry have been accumulated. Per-

haps part of these are not true and are harmful rather than helpful. Certainly in the case of "globulins" it is necessary to alter the present belief that by assigning the name "globulin" to a product it becomes a chemical entity. According to Table 1 it should be possible to isolate a series of globulins from wheat flour, the limit to number being only the number of salts and salt concentrations used for the extraction. That such a series of globulins exists is of course preposterous. If this be true for the "globulins" does it likewise hold for other protein classes? Certain evidence already available in this laboratory would make it appear that at least certain of the prolamines, which have been extensively studied and regarded as distinct entities, are not homogeneous, but can be readily fractionated by using the proper technique. The only questions are: *are these fractions homogeneous?* and *how can homogeneity be proven?* We must admit that we do not know. As to the other classes, only a systematic study, *in which all preconceived notions are obliterated,* can determine whether or not the classification is valid and of advantage to the study of proteins.

That our results with wheat flour are applicable to other protein-containing materials is evidenced by the data of Stiasny and Ackermann,[29] Stiasny,[30] Gustavson,[31] von Weimarn,[32] Thomas and Foster[33] and Thomas and Kelly,[34] where somewhat similar results have been obtained using gelatin, casein, silk fibroin, and collagen. Although all of these authors have observed that neutral inorganic salts peptize proteins to differing degrees, depending upon the nature of the anion or cation of the salts, no one, in so far as we are aware, has called attention to the interpretation of the results as bearing on the problem of protein classification, or questioned the definition of the term "globulin."

The Peptization Process.—Incidentally we wish to question the use of the term "hydrolysis" as used by Thomas and Foster[33] and Thomas and Kelly[34] for what we regard to be "peptization." Hydrolysis in the case of proteins should be reserved for the phenomenon whereby primary valence linkages in the protein molecule are opened by the addition of H_2O and an increase in free amino and carboxyl groups results. Such an increase in free $—NH_2$ and $—COOH$ groups does not appear to accompany such peptizations as we have been discussing. Thus Stiasny[30] reports that when gelatin is peptized by KCNS no true hydrolysis takes place, for he finds no increase in either free

[29] Stiasny, E. and Ackermann, W., "Ueber die Wirkung von Trypsin auf Kollagen und die Beeinflussung dieser Wirkung durch Neutralsalze." *Kolloidchem. Beihefte,* 17, 219-55 (1923).

[30] Stiasny, E., "Ueber der Einflusz von Neutralsalzen auf einige Eigenschaften der Gelatine." *Kolloid-Z.,* 35, 353-8 (1924).

[31] Gustavson, K. H., "Specific Ion Effects in the Behavior of Tanning Agents toward Collagen Treated with Neutral Salts." Colloid Symposium Monograph, vol. 4, 1926, pp. 79-101.

[32] Von Weimarn, P. P., "Conversion of Fibroin, Chitin, Casein and Similar Substances into a Ropy-Plastic State and Colloidal Solution." *Ind. Eng. Chem.,* 19, 109-10 (1927).

[33] Thomas, A. W. and Foster, S. B., "The Destructive and Preservative Effect of Neutral Salts upon Hide Substance." *Ind. Eng. Chem.,* 17, 1162-4 (1925).

[34] Thomas, A. W. and Kelly, M. W., "The Destructive and Preservative Effect of Neutral Salts upon Hide Substance II." *Ind. Eng. Chem.,* 19, 477-80 (1927).

amino groups or in free carboxyl groups. We have confirmed Stiasny in this respect and find that no increase in free amino groups occurs when gelatin or gliadin are peptized by $N/1$ KI, the protein being allowed to stand in contact with the salt solution for 24 hours and the KI being then removed by dialysis. The problem appears therefore to be primarily a colloidal problem and not one involving true hydrolysis. Stiasny notes that whereas he could readily peptize gelatin with KCNS, the reaction was apparently not completely reversible, inasmuch as the gelatin sol obtained after dialysis to remove the KCNS did not have the identical viscosity of the original gelatin sol. Such a result is perhaps to be expected in the light of the experiments of Gortner and Hoffman [35] where it was shown that the past history of a gelatin sol or gel was reflected in its subsequent colloidal behavior.

In our experiments 2 grams of gelatin were readily peptized by 50 cc. $N/1$ KI solution to form a relatively mobile sol, which set to a rigid gel when the KI had been removed by dialysis at constant volume. This fact, together with the fact that there was no increase in free —NH_2 groups, is taken as evidence that no true hydrolysis occurred, and that the only effect of the KI treatment was an increased peptization accompanied by a change in degree of hydration.

Can We Abandon the Colloid Viewpoint in Studying Protein Systems?—A great deal has been written in the last few years by Loeb and followers of the Loeb school, in which it has been insistently stated that the colloid viewpoint has hindered rather than advanced our knowledge of the physical chemistry of the proteins. It has been repeatedly emphasized that only well-known chemical laws are necessary to explain protein behavior and that the reactions of proteins with acids and bases are entirely stoichiometrical and can be fully explained by considering the hydrogen-ion concentration and the Donnan Equilibrium.

Hoffman and Gortner [36] as well as many others have presented evidence that adsorption plays a rôle in acid and alkali binding. Perhaps the most striking part of the data of Hoffman and Gortner is the marked *negative* temperature coefficient for acid and alkali binding. It is difficult to see how this can be reconciled with a purely stoichiometrical reaction of primary valences, whereas it is the logical expectation for an adsorption phenomenon.

We have seen in the present paper that variation in hydrogen-ion concentration does not account for the lyotropic series phenomena. We have seen that there are specific anion and cation effects exhibited by inorganic salt solutions of essentially identical ionic concentration. We have seen that these anion and cation effects are of sufficient magnitude

[35] Gortner, R. A. and Hoffman, W. F., "Evidence of a Structure in Gelatin gels," *Proc. Soc. Exper. Biol. Med.*, 19, 257-64 (1922).
[36] Hoffman, W. F. and Gortner, R. A., "Physico-Chemical Studies on Proteins. The Prolamines—Their Chemical Composition in Relation to Acid and Alkali Binding." Colloid Symposium Monograph, vol. 2, 1925, pp. 209-368.

to completely overshadow relatively large variations in hydrogen-ion concentration.

Accordingly there is left only the "Donnan Equilibrium" to be considered. We believe it is only necessary to quote two authorities in this connection. A. V. Hill[37] states "It is contended by Loeb that the Donnan Membrane Equilibrium, involving the presence of an indiffusible ion, is the basis of the colloidal properties of a protein solution. While the possibility of this conclusion is admitted, it is pointed out that one of the chief arguments employed in its favour by Loeb is incorrect. Loeb shows that the P. D. observed experimentally between a protein and a non-protein solution separated by a membrane agrees very exactly with that "calculated" from the difference in hydrogen-ion concentrations also observed experimentally, and concludes that this supports his theory. As a matter of fact, this equality is a necessary and inevitable consequence of the manner in which his observations were made and of general thermodynamical reasoning, and its proof is independent of any theory of the mechanism by which the P. D. is produced," and H. Rinde,[38] working in Donnan's laboratory, in a paper communicated to the Philosophical Society by Professor Donnan, states (after recalculating some of Loeb's data), "J. Loeb has, in his monograph 'Proteins and the Theory of Colloidal Behavior,' given an account of his experiments on gelatin. He thinks he has proved that gelatin gives a real chemical reaction with acids or bases. . . . It is evident that the theoretical values for the amount of adsorbed ions and the values calculated from determinations of the activities inside and outside the membrane check surprisingly well, and it is therefore very likely that the 'reaction' between gelatin and HCl is not a chemical reaction in the sense assumed by Loeb, but an adsorption process, and that the hydrogen ions are bound by means of residual valences to the gelatin particles. Exceptions from this may occur in the region of the isoelectric point, where a real chemical reaction may take place. Besides this adsorption of hydrogen ions there is also an adsorption of neutral HCl molecules, as can be calculated from Loeb's experimental results."

Chapman, Greenberg and Schmidt[39] have recently published data on the nature of the combination of certain acid dyes and proteins which they interpret as showing that there is a chemical combination of the dye with the protein, the reaction taking place in stoichiometrical proportions. One of us[40] has discussed their data and pointed out that their

[37] Hill, A. V., "The Potential Difference Occurring in a Donnan Equilibrium and the Theory of Colloidal Behavior." *Proc. Roy. Soc.*, **102A**, 705-10 (1923).

[38] Rinde, H., "A Method for the Determination of the Adsorption of Ions on Colloidal Particles by Means of Donnan's Membrane Equilibrium Theory." *Phil. Mag.* (7) 1, 32-50 (1926).

[39] Chapman, L. M., Greenberg, D. M., and Schmidt, C. L. A., "Studies on the Nature of the Combination between Certain Acid Dyes and Proteins." *J. Biol. Chem.*, 72, 707-729 (1927).

[40] Gortner, R. A., "The Nature of the Combination between Certain Acid Dyes and Proteins," *J. Biol. Chem.*, 74, 409-13 (1927).

findings are capable of an entirely different interpretation and as such offer a striking substantiation of the colloid theory.

It is pointed out that proteins in systems having a hydrogen-ion concentration greater than the pH of the isoelectric protein must exist as positively charged ionic micelles and that there would be an interaction between such ionic micelles and the dye anion so as to reduce the ζ potential to zero and cause flocculation of a protein-dye complex.

Chapman, Greenberg and Schmidt found that a constant amount of dye was necessary to flocculate a given amount of protein at all hydrogen-ion concentrations greater than pH 2.5 and because of this fact they argue for a reaction between primary valence forces. Gortner pointed out that it is not surprising that mutual precipitation reactions should be stoichiometrical, for stoichiometrical reactions are a necessity if we consider that the ζ potential at the interface must be reduced to zero before flocculation will occur and that when the ζ potential is reduced to zero, no further reaction between the dye and protein can take place. Thus, a constant amount of dye anion possessing a definite negative ζ potential will flocculate a definite amount of positively charged protein possessing a constant positive ζ potential and the reaction will not necessarily be a reaction between primary valence forces but can be regarded as entirely an electrokinetic phenomenon.

To explain the results of Chapman, Greenberg and Schmidt as well as many of the results of Loeb, it is only necessary to assume that the ζ potential on the protein micelle increases in magnitude up to a pH of 2.5 and thereafter remains constant for further increases in hydrogen-ion concentration, *i.e.*, the ionic micelle reaches its maximum charge at approximately pH = 2.5. Such an assumption would explain the increase in viscosity of protein sols between the isoelectric point to a maximum at approximately pH 2.5; *cf.* Gortner and Sharp.[41] The subsequent decrease in viscosity of protein sols at acidities greater than pH = 2.5 can be regarded as due to a dehydration of the ionic micelle without affecting the magnitude of the ζ potential. Kruyt [42] and Kruyt and de Jong [43] have shown that both the ζ potential and hydration are independent factors in governing the stability of lyophilic systems.

It may be well to point out here that the ζ potential is distinct from the ε or "phase boundary" potential. The "membrane potentials" which Loeb measured, and from a study of which he drew the conclusions that proteins were not reacting as colloids, were the ε potentials and while these determine the thermodynamic equilibrium, they in no way

[41] Gortner, R. A. and Sharp, P. F., "The Physico-Chemical Properties of Strong and Weak Flours, III. Viscosity as a Measure of Hydration Capacity and the Relation of the Hyrogen-Ion Concentration to Imbibition in the Different Acids; IV. The Influence of the Ash of Flours upon the Viscosity of Flour-in-Water Suspensions." *J. Phys. Chem.*, 27, 481-492 *and 567-576 (1923).*

[42] Kruyt, H. R., "Die Stabilitätsverhältnisse bei lyophilen Kolloiden." *Koll. Z.*, 31, 338-341 (1922).

[43] Kruyt, H. R. and De Jong, H. G., "Kapillarelektrische Erscheinungen an lyophilen Solen." *Z. physik. Chem.*, 100, 250-265 (1922).

affect the colloidal behavior of the system or colloidal stability. The ζ potential, on the other hand, is concerned only with surface forces and the magnitude and sign of the ζ potential (together with hydration) determine the stability of colloid systems and colloidal behavior such as adsorption, flocculation, mutual precipitation, and all of the electrokinetic phenomena characteristic of colloids.

Just why certain workers should accept the viewpoint that aqueous systems of starches, cellulose, rubber, and other lyophilic and lyophobic systems may react as colloids but that proteins are characterized by an entirely different behavior is incomprehensible. However, even Loeb's data are capable of more than one interpretation, as is indicated by the cited comments of Rinde [38] and Hill,[37] and the fact that a lyotropic series exists, which Loeb [20] admits would not be explainable by his theory, makes it essential that we use all of the tools of research which we possess, in our study of protein systems. We know that the protein molecule is large enough to bring the size of the particles well within the boundary of the colloid realm. We believe that, with the exception of the albumins, most proteins exist in "solution" as micelles. If there are electrokinetic forces at interfaces between water and starch, cellulose, or glass, there must be electrokinetic forces at the interfaces of a protein-water system and to ignore such forces is only to delay a full and complete understanding of protein behavior.

Summary

A study has been made of the peptizing effect of aqueous solutions of 21 inorganic salts on the proteins of wheat flour. Most of these salts were used in several concentrations, ranging from 0.5 N to 2.0 N. The following conclusions have been reached.

1. There is a pronounced lyotropic or Hofmeister series of anions arranging themselves in the order of increasing peptizing effect of F $<$ SO_4 $<$ Cl $<$ tartarate $<$ Br $<$ I.

2. There is a less pronounced, but still distinct, lyotropic series of cations, in order of increasing peptization of Na $<$ K $<$ Li $<$ Ba $<$ Sr $<$ Mg $<$ Ca.

3. Hydrogen-ion concentration differences do not account for these lyotropic series. The lyotropic effects are due to the properties of the anion and cation of the salt and are observable and measurable even at constant hydrogen-ion concentration.

4. The alkali halides all cause decreasing peptization with increased salt concentration.

5. The halides of the alkaline earths as a rule cause increased peptization with increasing salt concentration. This is particularly noticeable for $MgCl_2$, $MgBr_2$, $SrCl_2$ and $CaBr_2$ solutions.

6. Our data show that protein "solubility" in neutral salt solutions

is, in reality, protein peptization, and as such it is governed as to rate and extent by the nature of the particular anions or cations present in the salt solution.

7. Inasmuch as globulins are defined as "proteins soluble in dilute solutions of salts of strong acids with strong bases" we wish to raise the questions, *what salts, what dilutions,* and lastly, *what is a globulin?*

8. Our data show that $N/1$ solutions of KF extract an average of 13 per cent, KCl 23 per cent, KBr 37 per cent and KI 64 per cent of protein from wheat flours. Which salt extracts the globulins? We do not believe that any salt used, in any one of the concentrations, extracts a chemical entity which should be designated by the term "globulin."

9. "Peptization" by neutral salt solutions is not "hydrolysis" for there is no increase in free amino or carboxyl groups.

10. It is pointed out that the colloid chemical viewpoint still affords the most satisfactory explanation for many of the properties of protein systems.

Division of Agricultural Biochemistry,
University of Minnesota,
St. Paul, Minnesota.

RELATION OF HYDROPHILIC COLLOIDS TO WINTER HARDINESS OF INSECTS [1]

By William Robinson

Introduction

Resistance to low temperatures in cultivated plants, being a desirable quality, is investigated by physiologists and geneticists in connection with the breeding of cold-hardy varieties. Winter hardiness in animals, especially cold-blooded animals, is of equal interest, but the ultimate object of the entomologist, for instance, is just the reverse of that of the plant breeder. Low temperatures of winter provide an effective means of natural control of insect pests, and the entomologist studies the subject chiefly from that standpoint.

Injurious species may be very numerous in the summer and autumn and proportionately scarce in the following spring. Low temperature as a means of control is effective in two ways. It reduces the numbers of individuals year after year even in an environment in which the species has become established, and it restricts very largely the insects' further spread. While their hosts go onward, the migration of many species of injurious insects is checked by the winter even when the summer is warm enough to permit development of a life cycle.

Why some species are unable to prepare themselves for certain low temperatures of winter and are thereby killed outright if so exposed, while other species are able to survive, is a problem about which not much is known. In the field of colloid chemistry, however, there appears to be at least a partial solution of the problem in the activities of hydrophilic colloids.

Historical

On the Evidence for the Existence of Bound Water in a Hydrophilic Colloid System.—It is through the study of adsorption phenomena, which are associated with colloidal activities, that much of the evidence for the existence of bound water has been obtained. The hydrophilic or "water-loving" colloids form a large part of the total colloids found in biological tissue. As their name implies, they have a strong attraction for water. This water is formed or bound on the

[1] Published with the approval of the Director as Paper No. 703 of the Journal Series of the Univ. Minn. Agr. Exp. Station.

surface of the colloidal particles as a film or shell, and may be greater in diameter than the particle itself. The force with which these layers of water are held by the particle is almost inconceivable in biology.

Harkins and Ewing[2] as cited by Gortner[3] have presented some of the most striking evidence for the forces of attraction between water and an organic material. They found that when 10 grams of dry (ignited) charcoal was treated with 1 gram of water, the water was attracted onto the surface by an attractive force equivalent to a pressure of 37,000 atmospheres, and that under this pressure the water was compressed to 75 percent of its original bulk. Neuhausen and Patrick[4] have presented somewhat similar evidence for the compression of water on the surfaces of silica gel (colloidal SiO_2). The water is held so firmly on the surfaces that 4.8 percent of water still remains after heating the gel at 300° for 6 hours in a complete vacuum.

Boswell and Dilworth,[5] again cited by Gortner,[3] also made a study of the force with which water is held on the surface of an aluminium oxide gel. To account for the tremendous compression which takes place, these authors postulated that the water is oriented on the surfaces of the colloidal particles as layers of hydrogen and hydroxyl ions.

Both the living cells and the intercellular liquids, as is now well known, contain countless millions of colloidal particles. Hofmeister has calculated that one liver cell contains:

225,000 billion molecules of water,
53 billion molecules of protein (molecular weight = 16,000)
166 billion molecules of fats or lipoids (molecular weight = 166)
2,900 billion molecules of crystalloids.

Gortner[3] states: "It has for a long time been recognized that the proteins are in the colloidal state and contribute to the surface reactions of the system. The fats and lipoids are either colloidally dispersed or are in the form of emulsions, where the reactions are those characteristic of surfaces and interfaces, but I do not believe that sufficient emphasis has been placed upon the fact that *the water and the crystalloids may likewise exist largely in the colloidal state.* In other words, whenever we have colloidal material in an aqueous medium, we will find that a certain amount of the water is 'bound' on the surfaces of the colloidal particles and the amount which is bound is not a fixed quantity but varies greatly from time to time as the system or the conditions are changed."

[2] Harkins, W. D., and Ewing, D. T., "A high pressure due to adsorption and the density and volume relations of charcoal," *J. Am. Chem. Soc.*, **43**, 1787-1802 (1921).
[3] Gortner, R. A., "Adsorption and vital phenomena." *Mayo Foundation Lectures* 1925-6. In press.
[4] Neuhausen, B. S., and Patrick, W. A., "Organgels of silicic acid," *J. Am. Chem. Soc.*, **43**, 1844-6 (1921).
[5] Boswell, M. C., and Dilworth H. M., "On the mechanism of catalysis by aluminium oxide," *J. Phys. Chem.*, **29**, 1489-1506 (1925).

On the Evidence that Bound Water Is Related to Winter Hardiness.—Several investigators, namely, Hooker,[6] Rosa,[7] Strausbaugh,[8] Newton and Gortner,[9] Newton,[10] and Dunn and Bakke,[11] when working with plants, found a direct relation between winter hardiness of plant tissues and hydrophilic colloid content.

Newton [10] when studying frost resistance in winter wheat, found that the hardier the variety of wheat plant the more hydrophilic colloids were present in the press juice. He also noted that associated with this there was a direct relationship between cold hardiness and imbibition pressure of the wheat leaves. That is, under a falling temperature the hydrophilic colloids in the plant sap adsorbed free water in direct proportion to the hardiness of the plant; and Newton was able to measure the cold resistance of the wheat plant, qualitatively, in the laboratory.

Experimental

The Problem.—The adsorption of water under a falling temperature, whereby water is removed from the free and changed into the bound form, is of undoubted importance and significance to plants growing in the colder regions. The advantages to the species of having part of its water content transformed in this way is discussed more fully later. Such protection against the cold of winter would be of much importance in the animal kingdom as well; and the writer therefore conducted a series of experiments, Robinson,[12] to determine if the phenomenon observed by Newton for plant tissues would hold also for animal tissues, particularly those of cold-blooded animals such as insects.

The Method.—In making his determinations, Newton used 100 grams of hardened wheat leaves and squeezed out the plant juice under a known pressure. In that way he established a correlation between pressure applied and amount of liquid expressed. That method, while suitable for plants, cannot very well be used for insects because such a large mass of material is rarely available. The method used by the writer was a modification of the method of Thoenes,[13] which is based on the fact that at — 20° C. none of the bound water but all of the free water will be frozen. With this method it is possible, with the use of a

[6] Hooker, H. D., Jr., "Pentosan content in relation to winter hardiness," *Proc. Am. Soc. Hort. Sci.*, 17, 204-207 (1921).

[7] Rosa, J. T., Jr., "Investigations on the hardening process in vegetable plants." *Mo. Agr. Exp. Sta.* Res. Bul. 48 (1921); "Pentosan content in relation to hardiness in vegetable plants." *Proc. Am. Soc. Hort. Sci.*, 1920, pp. 207-210.

[8] Strausbaugh, P. D., "Dormancy and hardiness in the plum." *Bot. Gaz.*, 71, 337-357 (1921).

[9] Newton, R., and Gortner, R. A., "A method for estimating the hydrophilic colloid content of expressed plant tissue fluids," *Bot. Gaz.*, 74, 442-446 (1922).

[10] Newton, R., "The nature and practical measurement of frost resistance in winter wheat." *Univ. Alberta. Coll. of Agr.* Res. Bul. 1 (1924).

[11] Dunn, S., and Bakke, A. L., "Adsorption as a means of determining relative hardiness in the apple," *Plant Physiol.*, 1, 165-178 (1926).

[12] Robinson, W., "Water binding capacity of colloids a definite factor in winter hardiness of insects," *J. Econ. Ent.*, 20, 80-88 (1927).

[13] Thoenes, F., "Untersuchungen zur Frage der Wasserbindung in Kolloiden und tierischen Geweben." *Biochem. Z.*, 157, 174-186 (1925).

calorimeter, to measure the free water through its heat of fusion. The value for free water thus obtained is subtracted from the total water which is found by desiccation at 100° C., and the remainder is regarded as bound water. At this temperature all the bound water cannot be removed and a higher drying temperature cannot safely be used with biological tissue, so *the bound water determinations have always a minimum value.*

The heat-of-fusion method of measuring the free and bound water, as adapted by the writer to the present series of experiments, is given in detail below.

The calorimeter used consists of a single Dewar flask with inside dimensions five inches high and one inch in diameter. The flask was prepared with a very high vacuum, but the inner walls were not silvered (which is done to prevent radiation of heat) because visibility is necessary in order to keep the material down below the surface of the water. The calorimeter was placed, for support, in a heavy, flat-bottomed container.

A thermo-electric couple was used to determine the temperature of the water in the calorimeter, but a mercury thermometer marked in tenths of a degree may be used. If the thermocouple is employed it should be made preferably of enamelled wire. The warm junction end should be slightly modified by running it down through a piece of glass tubing until it extends beyond the end about 2 mm.; then the end of the tube should be closed with sealing wax, leaving the warm junction itself just outside the tube. The end of the glass tube should be lipped slightly all around to aid in mixing up the water.

Whether using the thermocouple or thermometer, the opening at the top of the flask should be fitted with a cork to prevent convection currents within the calorimeter. A hole, large enough to permit free movement of the thermocouple or thermometer, should be bored in this cork and covered with a piece of sheet rubber with a slit in it. This allows the thermocouple or thermometer to be inserted and to be moved about when stirring up the water in the flask.

When ready to make a determination, the material, usually about one gram in weight, is weighed in milligrams on an analytical balance. It is then put into a numbered container which is afterwards corked to prevent evaporation, and placed in the refrigerating cabinet at about — 20° C. for several hours to ensure thorough freezing. When the free water determination is to be made, the required amount of water is poured into the calorimeter. The writer always uses 10 cc. The water should be a few degrees above room temperature. Then the water is stirred to bring it into equilibrium with the calorimeter; and, while still stirring, the temperature of the water is taken. Next the material in its closed container is taken from the refrigerator and, without touching it with the fingers, the material is dropped quickly from the container

into the water of the calorimeter. The cork is then replaced in the flask, and the water stirred briskly but not enough to splash any upon the sides of the flask, as this causes large errors in measurement. The temperature of the water should be watched carefully and as soon as it ceases to drop the temperature should be taken. The material is then removed and placed in an oven to desiccate at 100° C. for several hours until it ceases to lose weight. Following this the material is finally weighed.

Calculation of the amount of free water within the material is made according to the following formula:

$$X = \frac{FN(T_3 - T_4) - SW(T_2 + T_4)}{80 - \frac{T_2 - T_1}{2}}$$

where N is the volume in cc. of water in the calorimeter; T_3 is the temperature of the water in the calorimeter at the beginning of the test; T_4 is the temperature of the water in the calorimeter at the end of the test; S is the specific heat of the material, and this is easily obtained with the calorimeter by following the procedure given in most text-books in physics; T_2 is the temperature of the material at the beginning of the test. It is, of course, below zero and thus it has a minus sign. However, this sign should be disregarded and T_4 should be added to it and T_1 subtracted from it, as though it were plus. T_1 is the average freezing point of similar material. Neither the freezing point nor the specific heat should be obtained for the identical mass under determination but for other masses of similar material. The reason for this is evident.

F is a correction factor which it has been found necessary by the writer to use in the formula. The drop in the temperature of the water in the calorimeter does not give the full value of the heat of fusion. The explanation is that the heat absorbed by the melting ice is taken not only from the water but also from the walls of the calorimeter and the thermometer in contact with that water. The value obtained for heat of fusion is therefore not so large as it should be, and a correction must be made. This is an easy thing to make; and the correction factor should be determined for each calorimeter made.

To ascertain the correction factor, it is only necessary to make several tests of the flask with samples of known weight of ice from pure water and to determine, on the basis of 80 calories of heat per gram of ice, how much heat is taken up other than from the water in the calorimeter. The calculation for free water, when made with the formula without using the factor F, will give a value too low. Then, knowing the weight of ice, the expression $N(T_3 - T_4)$ should be multiplied by an amount sufficient to bring the value for heat up to its full value. This amount then is the correction factor for that particular deter-

mination. It is necessary, however, to use several samples of ice and of various weights, because a slight experimental error occurs in this heat-of-fusion method and because the larger the volume the greater the area of glass that will be in contact with the water of the calorimeter and thus the greater gain of heat by the water. However, when the results are charted as in Figure 1 a definite correlation will be obtained, and it will then be easy to find the correction factor by interpolation for any weight of material subsequently used.

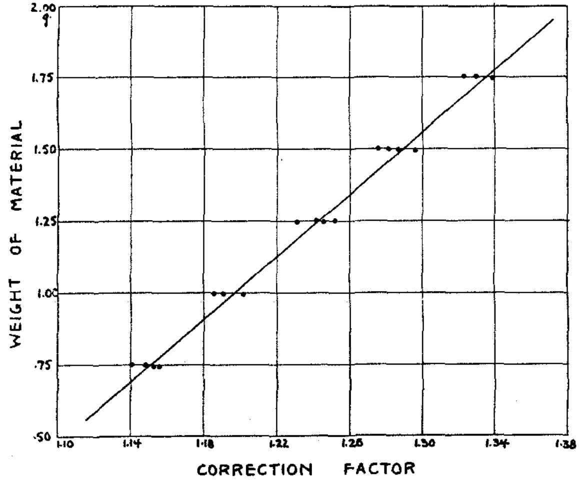


FIG. 1.—Sample of chart to be made for finding correction factor of calorimeter.

To obtain masses of ice of known weight it has been found satisfactory to use containers, other than glass, of known weight and specific heat and to measure into the containers the required amounts of water. The writer uses tinfoil which has a specific heat of 0.05, and the containers are made by cutting the tinfoil into squares and pressing them individually around the base of a test-tube. When the containers are made, the water is measured into them and frozen. In making the determinations of heat of fusion, the ice and tinfoil container are dropped into the calorimeter together. A slight addition to the formula, on account of the tinfoil container, is necessary, as follows:

$$X = \frac{FN(T_3 - T_4) - [SW(T_2 + T_4) + S_1W_1(T_2 + T_4)]}{80 - \frac{T_2 - T_1}{2}}$$

where, in addition to the other symbols, S_1 is the specific heat and W_1 is the weight of the container.

The freezing point of the free water of biological tissue is practically always lower than 0° C., sometimes being as low as —18° C. Therefore to allow for this fact, it is necessary to use the expression $T_2 - T_1$ as shown in the formula, when allowing for the change in specific heat of the material at the time the ice within the tissue melts.

Apart from the foregoing modifications, the formula used in these experiments is similar to that employed by Thoenes. In his article Thoenes has developed his equations and given the reasons for arriving at his formula. The reader is referred to that article for such details.[13]

The Material

Among the insects used was a cold-hardy species, the Promethea Moth called *Callosamia promethea,* which passes the winter in a cocoon attached to the twigs of shrubs. This species is therefore exposed to the low temperatures of our northern winters.

The second type was a soil inhabiting insect called the "White Grub" belonging to the genus *Phyllophaga* which occurs in the northern states. Upon the approach of winter this insect moves down through the soil ahead of the frost, but it is frequently found near the frost line.

The third species used was the extremely non-hardy Granary Weevil called *Sitophilus granarius.* This is believed to be a tropical species and to have spread to the temperate zones, and to exist there, in the stored grain upon which it feeds. The temperature of stored grain rarely goes below 7° C. during winter or summer and it is usually much higher. It therefore provides ample protection from the low temperatures of the north. An exposure to 2° C. for one month, as shown by Robinson,[14] would be fatal to this species.

Artificial hardening of the material was done in the refrigerating cabinets of the laboratory of the Division of Entomology of the University of Minnesota. The cabinets were made by the Carrier Engineering Corporation. They are equipped with very sensitive electric control of temperature and humidity and can be operated for weeks at temperatures varying less than one degree. The low temperatures were obtained by expansion of ammonia gas and a York two-ton automatic refrigerating machine was used.

[14] Robinson, W., "Low temperature and moisture as factors in the ecology of the rice weevil, Sitophilus oryza, and the granary weevil, Sitophilus granarius," *Univ. Minn. Ag. Exp. Sta.* Tech. Bul. 41 (1926).

The Experimental Data

As the experiments progressed, it was seen that the phenomenon observed by Newton [10] for wheat plants was holding true also for animals such as insects. Under the stress of a falling temperature the hardy Promethea began to gain in adsorbed or bound water and to lose in free water; the more or less neutral White Grubs remained practically unchanged; while the non-hardy Granary Weevils actually lost in bound and gained in free water; thus establishing a direct correlation between winter hardiness and amount of bound water.

Considerable difference in total weight was found, especially among the different species. Therefore in order to present data which could be comparable a unit total weight of one gram of material was taken. In the case of the Granary Weevil as many as 400 individuals were required for each test.

Table 1.—Total, Free and Bound Water Content of Promethea.

Length of Exposure Days	Temperature °C.	Total Water Mg.	Free Water Mg.	Bound Water Mg.
Start	+18	682	619	63
Start	+18	703	651	52
Start	+18	689	627	62
5	−10	668	481	187
5	−10	697	503	194
8	−12	678	433	245
8	−12	704	450	254
12	−14	691	477	214
12	−14	695	410	285
14	−14	683	406	277
14	−14	708	410	298
14	−14	698	447	251
16	−14	680	408	272
16	−14	688	403	285
17	−14	716	451	265
18	−14	690	422	268
18	−14	696	378	318
21	−14	701	401	300
21	−14	706	452	254
23	−14	684	384	263
23	−14	713	453	260
32	−14	709	384	315
35	−14	716	391	325
35	−14	712	425	287
40	−14	701	390	311
40	−14	692	401	291
44	−14	719	429	290
49	−14	699	378	321
49	−14	701	421	280

Table 1 and Figure 2 show the data secured for the hardy Promethea. It will be observed that an increase in bound water from 52 mg. to 320

mg. occurred with this species, and that this was practically coincident with the fall in temperature. The refrigerating cabinet was held from the tenth day to the end of the experiment at — 14° C. which was just above the temperature at which the insects would freeze. It is probably worth mentioning here that the average freezing point of the

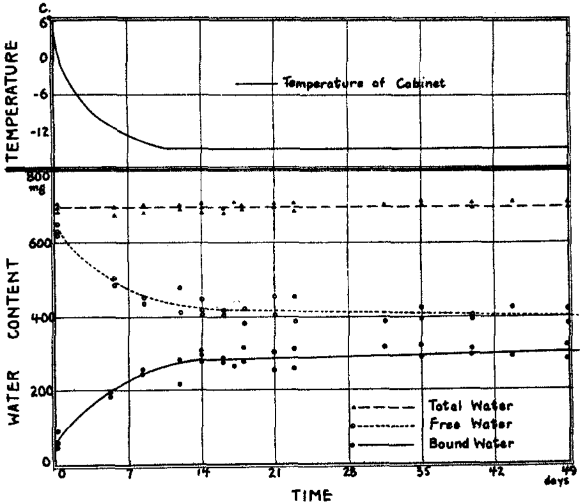


FIG. 2.—Total, free and bound water content of Promethea.

free water, throughout the experiments, was — 2.5° C. The reason for the fact that the outside temperature could be lowered down to — 14° C. without freezing taking place is that the internal temperature of the insects was always higher than the freezing-point or at least higher than the undercooling point of the body liquids.

The difference between the temperature of the cabinet and that of the insects themselves, is shown in Table 2. The determinations are for different individuals taken during the experiments. The interval between the first and the last temperature determinations was about three weeks. It was during this same period that adsorption was at its maximum (*See* Fig. 2). The source of heat of Promethea was partly from its metabolic processes, but this was undoubtedly slight; it is more probable that most of the heat was derived from the process of imbibi-

TABLE 2.—COMPARISON OF TEMPERATURE OF CABINET WITH INTERNAL TEMPERATURE OF PROMETHEA.

Cabinet Temperature ° C.	Internal Temperature of Insects
+ 7.0	+ 7.0
— 2.0	+ 2.0
— 2.0	+ 2.5
— 3.5	+ 1.5
— 3.5	+ 2.0
— 10.0	+ 2.0
— 10.0	+ 2.0
— 11.0	+ 1.0
— 11.0	+ 1.0
— 11.0	+ 2.0
— 14.0	— 3.0
— 14.0	— 3.0
— 14.0	— 5.0
— 14.0	— 6.5

tion. Gortner [3] states "When a gel imbibes water there is a contraction of the system, i.e. the gel + water occupies less volume than they occupied separately. Water is compressed; heat is generated. Swelling and solution are not identical. Swelling (imbibition) of gelatin liberates heat; solution (dispersion) of gelatin absorbs heat. From the heat which is liberated, it is possible to reconstruct the imbibition curve." When the present experiments were undertaken, it had not been planned to determine rate of respiration or heat of imbibition, so that the part played by each in this instance is unknown.

With further reference to Table 1 and Figure 2, some individuals not recorded therein were allowed to freeze and adsorption with them then ceased.

TABLE 3.—TOTAL, FREE AND BOUND WATER CONTENT OF WHITE GRUBS.

Length of Exposure	Temperature	Total Water	Free Water	Bound Water
Days	° C.	Mg.	Mg.	Mg.
Start	+ 21	730	672	58
Start	21	814	736	78
Start	21	805	714	91
Start	21	736	653	83
Start	21	803	719	84
42	0.5	792	709	83
42	0.5	791	687	104
42	0.5	798	705	93
49	0.0	802	716	86
49	0.0	740	654	86
49	0.0	807	699	108
49	0.0	758	644	114
70	—2.0	800	686	114
70	—2.0	804	679	125
70	—2.0	813	718	95
70	—2.0	799	705	94

It is therefore probable that the maximum adsorption of this species is about 300 mg. or about 45 per cent of its total water content. The total weight and water remained practically constant throughout the experiments, which indicates that the rate of respiration, when the individuals were dormant, was very low. This is typical of cold resistant forms of wheat plants, as shown by Martin [15] and is probably true also for insects.

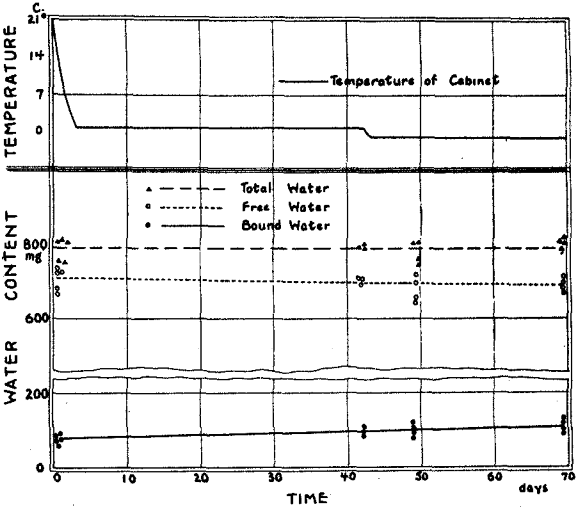


FIG. 3.—Total, free and bound water content of White Grubs.

Figure 3 and Table 3 show, for the White Grubs, the relations between bound and free water which were very slightly changed during a period of 10 weeks. The temperature was lowered nearly to the limit of their endurance, namely to —1.5° C. With this species, freezing was fatal in every instance observed, whereas the hardy Promethea was able to survive repeated freezing. Ten weeks' exposure of the White Grubs to a temperature close to their absolute minimum resulted in a very slow increase in bound water from about 80 mg. to 110 mg., an increase of about 3 per cent.

[15] Martin, J. H., "Comparative studies of hardiness in wheat." In press.

In the case of the non-hardy Granary Weevils (Fig. 4) the reverse of the effect shown in Figure 2 is seen. The temperature in this experiment was held at 0° C. A rapid drop in bound water occurred during the first 4 days, and death began to take place in 18 days. This species cannot endure dormancy even above the freezing point of water, as shown by Robinson.[14] The total water, charted in Figure 7 and total

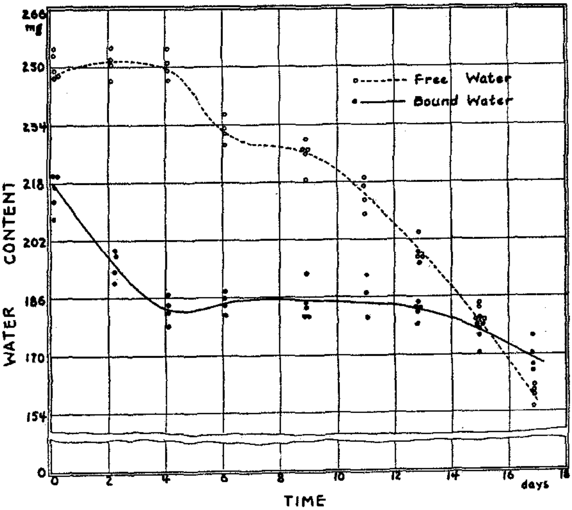


FIG. 4.—Free and bound water content of Granary Weevils.

weight, Figure 8, fell continually throughout the exposure. This indicates a relatively high rate of respiration during dormancy, a characteristic of non-hardy forms. It also indicates a change in the colloid structure of the protoplasm whereby syneresis (?) takes place at low temperature and bound water is transformed into free water.

DISCUSSION

As noted by Newton [10] for plants, there is no correlation between winter hardiness and activity of hydrophilic colloids when the material is in the unhardened condition. My own data show, for instance, that

TABLE 4.—TOTAL, FREE AND BOUND WATER OF *Sitophilus granarius*.

Length of Exposure Days	Temperature ° C.	Total Water Mg.	Free Water Mg.	Bound Water Mg.
Start	+20	466	253	213
Start	20	463	255	208
Start	20	469	249	220
Start	20	467	247	220
Start	20	464	247	217
2	0.0	458	257	199
2	0.0	441	251	190
2	0.0	444	246	198
2	0.0	445	252	193
4	0.0	433	249	184
4	0.0	433	255	178
4	0.0	433	246	187
4	0.0	433	251	182
6	0.0	418	237	181
6	0.0	420	232	188
6	0.0	412	228	184
6	0.0	419	233	186
9	0.0	411	218	193
9	0.0	410	227	183
9	0.0	411	227	184
9	0.0	407	227	180
9	0.0	410	230	180
11	0.0	400	213	187
11	0.0	399	219	180
11	0.0	395	217	178
11	0.0	399	207	192
13	0.0	379	195	184
13	0.0	380	198	182
13	0.0	380	197	183
13	0.0	382	204	178
13	0.0	380	197	183
15	0.0	358	183	175
15	0.0	358	178	180
15	0.0	357	179	178
15	0.0	356	179	177
17	0.0	327	160	167
17	0.0	329	159	170
17	0.0	330	155	175
17	0.0	322	161	165

before exposure to low temperature the hardy Promethea had only 10 per cent of bound water while the non-hardy Granary Weevil had 45 per cent of its total water content adsorbed. The correlation exists only when the organisms are subjected to the stress of winter conditions. But following hardening of the tissue the correlation between adsorption of water and winter hardiness is evident from the data submitted.

It seems possible that the direct relation between resistance to low temperatures and adsorption of water by hydrophilic colloids is of more importance than to serve merely as a measure of winter hardiness of an organism. It is probable that winter hardiness is itself due partly to the adsorption phenomenon. Some of the properties of water are

changed when it undergoes adsorption, and there may be some significance in this fact. Free water is practically incompressible, but Harkins and Ewing [2] found that under the attractive force of adsorption the bound water was compressed to 75 per cent of its original bulk. Newton and Gortner [9] found that bound water would not dissolve cane sugar. Thoenes [13] stated that bound water will not freeze at —20° C. The writer will present data later in this paper to show that bound water will not permit the conduction of an electric current. It may also be possible that bound water retards or prevents enzymic activity.

Studies of the effects of low temperature upon living tissue have brought out, among others, the following theories to account for injury or death.

(1) Freezing of body liquids in the intercellular spaces, with possible disruption of tissues by expansion of water during freezing.

(2) Desiccation of tissues and protoplasm due to the streaming of free water from the cells to the crystallization centers to restore equilibrium. (Syneresis of protoplasm?)

(3) Extreme concentration of salts in the tissues.

(4) Precipitation of proteins due to increased concentration of salts.

(5) Consumption of tissues due to persistence in the rate of respiration and inability of the organism, being dormant, to feed itself. Robinson.[14]

Reviews of the literature on the effects of low temperatures are presented concisely in the work of Abbe,[16] Wiegand,[17] Blackman,[18] Chandler,[19] Rosa,[7] Newton,[10] Payne,[20] Dunn and Bakke,[11] and Hildreth.[21]

Since bound water will not freeze at comparatively low temperatures, it seems evident that the greater the amount that can be converted into that form the greater will be the protection afforded to that species.

The imbibition pressure of adsorbed water is frequently very great, and amounts in some cases to several hundred or even thousand atmospheres of pressure, as shown by Harkins and Ewing,[2] Newton,[10] and Gortner.[22] The force with which this bound water is held serves largely to counteract the pull of water from the protoplasm during crystallization. The imbibition pressure, therefore, retards desiccation and consequent injury to the protoplasm.

When water is adsorbed there is a contraction of the system, as

[16] Abbe, C., "Influence of cold on plants. A résumé," *Exp. Sta. Rec.*, 6, 777-782 (1895).
[17] Wiegand, K. M., "The occurrence of ice in plant tissues." *The Plant World*, 9, 25-38 (1906).
[18] Blackman, F. F., "Vegetation and frost," *New Phyt.*, 8, 354-368 (1909).
[19] Chandler, W. H., "The killing of plant tissue by low temperature." *Mo. Agr. Exp. Sta. Res. Bul.* 8 (1913).
[20] Payne, N. M., "Freezing and survival of insects at low temperatures." *Quart. Rev. Biol.*, 1, 270-282 (1926).
[21] Hildreth, A. C., "Determination of hardiness in apple varieties and the relation of some factors to cold resistance," *Univ. Minn. Ag. Exp. Sta.* Tech. Bul. 42 (1926).
[22] Gortner, R. A., "Outlines of biochemistry, for students of the biological sciences." Mimeograph edition, University of Minnesota, 1925.

shown by Harkins and Ewing, where the colloidal particles and the water together occupy less space than the two separately. This contraction may serve to offset partly the effect of the expansion of water when freezing.

During adsorption there may be another means of protection from freezing in the depression of the freezing point due to the concentration of salts in the free water. Payne [20] made freezing point determinations throughout the year of oak borers which live beneath the bark of oak trees and are thus exposed to the lowest temperatures of winter.

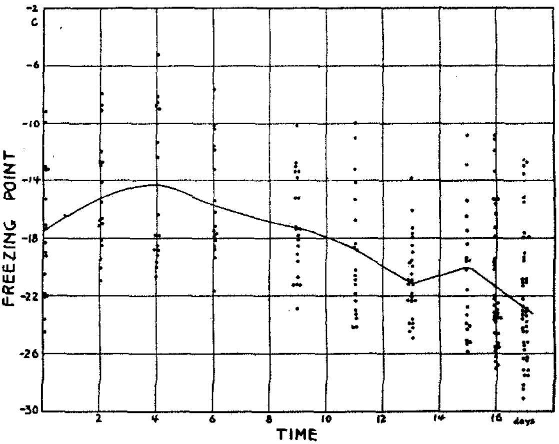


FIG. 5.—Freezing point of body liquids of Granary Weevils.

This author observed that during spring and summer the freezing point was raised and, as the autumn and winter approached, the freezing point of the free water of these insects was correspondingly lowered. This may be due to adsorption of water, and is undoubtedly an advantage to those species.

However, depression of freezing point upon the approach of winter is apparently not an essential factor in the hardening process, and it does not always accompany adsorption of water. In the case of Promethea used in the present experiments, the freezing point of the free water was not lowered and remained at an average of — 2.5° C. throughout the experiment, although from 40 to 45 per cent of the water was bound by the hydrophilic colloids. This is most likely due in part to

selective adsorption. Under some conditions both water and salts will be taken up, while under others the salts will be left in solution. If, for instance, the electric charges on the colloidal particles and on the salts are similar they will repel each other and adsorption of the salts will be opposed. If the charges are dissimilar the colloids and salts will be attracted and adsorption of the salts will be facilitated. Water and salts are adsorbed independently of each other and at different

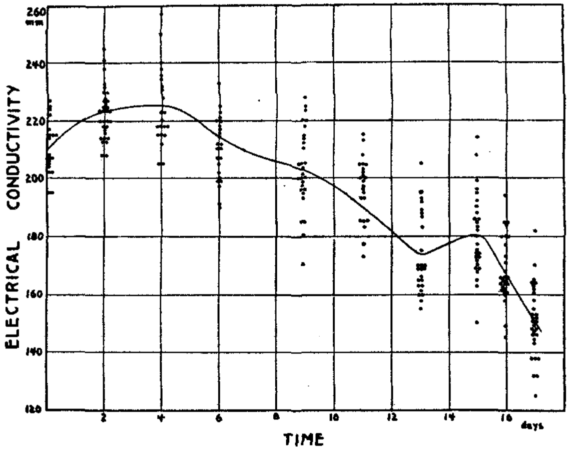


FIG. 6.—Electrical conductivity of body liquids of Granary Weevils.

rates. Therefore, depression of freezing point, even when it occurs, cannot necessarily be taken as an indication of the extent to which hardening has progressed.

If considering only freezing point depression, there would be evidence in Figure 5 of hardening with the Granary Weevil. However, this species has been shown (Fig. 4) to undergo the reverse of hardening under low temperature. The freezing points were taken simultaneously with determinations of bound and free water; and the bound water was shown to decrease from the beginning of the experiment until death occurred. The depression is therefore due, not to adsorption of water but to water loss through evaporation and respiration. There is similarity in Figures 4, 5, 6 and 9 which show data secured from the Weevils during the same series of experiments. During the

first four days of exposure this species suffered a rapid disruption of the gel structure (Fig. 4). Ordinarily this species exists with about 45 per cent of its total water in the bound condition. This is probably associated with the fact that its food contains only between 10 and 14 per cent of moisture and that this large amount of bound water is a mechanism for water conservation. However, a discussion of this subject will be reserved for a subsequent paper.

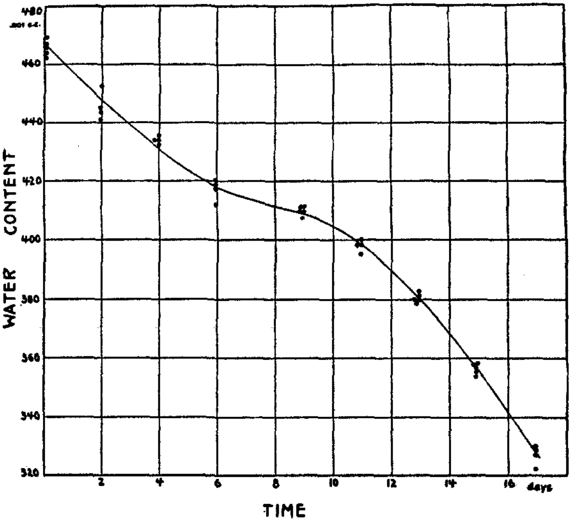


FIG. 7.—Total water content of Granary Weevils.

During the disruption of the gel structure the hydrophilic colloids lose their capacity to hold so much water and liberate it in the free condition. Thus during the first four days the rapid drop in bound water (Fig. 4) is accompanied by an elevation of the freezing point of the free water (Fig. 5) and a corresponding increase in electrical conductivity (Fig. 6). It is also associated with a marked increase in per cent of free water (Fig. 9). This marked increase in free water is shown also in Figure 4 but not so well as in Figure 9 because the actual amount of

free water is so strongly affected by the general decrease in total water as shown in Figure 7.

From the 4th to the 13th days there was very little change in the bound water but a rapid drop in free water (Fig. 4). This is also indicated by the depression of freezing point and decrease of electrical conductivity. The remarkably low freezing points of the body liquids toward the end of the experiments are abnormal and, as mentioned before, are due to desiccation of the tissues by evaporation. This was followed by death beginning on the 18th day of exposure.

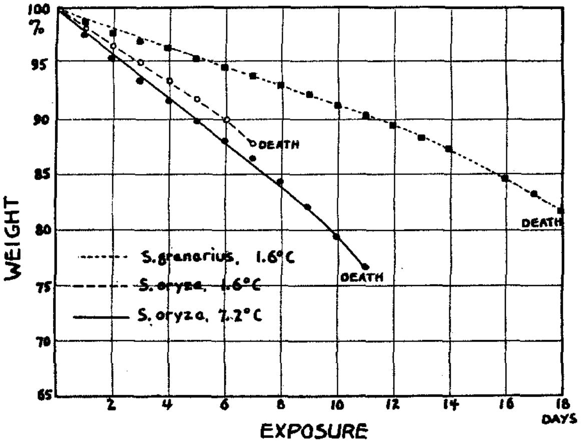


Fig. 8.—Loss of total weight of Granary Weevils during exposure to 1.6° C. From Univ. Minn. Ag. Exp. Sta. Tech. Bull. 41.

The close similarity of curves shown in Figures 4, 5, 6 and 9 tends to confirm the statement made by the writer elsewhere,[23] that, other things being equal, the electrical conductivity of living tissue varies directly as its free water content. Also the dissimilarity between those curves and that in Figure 7 appears to support this view and to indicate that bound water will not conduct a current of electricity. If the amount of bound water is small or remains constant within narrow limits, then the electrical conductivity of living tissue will be directly proportionate to the total moisture content.

[23] Robinson, W., "An electric method of determining the moisture content of living tissues," *Ecology*, 7, 365-370 (1926).

Any given species, when exposed normally to low temperatures, will probably react in a regular and definite manner according to the specific characteristics of its hydrophilic colloids. These, as is known, vary greatly in different organisms. Species may have definite, inherent limitations beyond which they cannot go. Low temperature is not, of course, the only factor involved in limiting distribution; but if the temperature encountered is lower than can be tolerated by the species then, by Liebig's "Law of Minimum" as pointed out by Chapman,[14] that is the limiting factor, no matter how favorable other factors may be. In

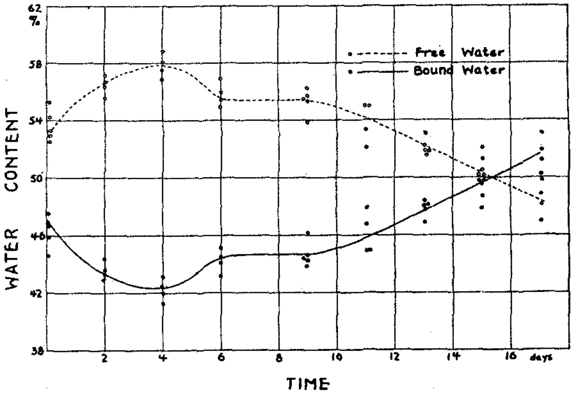


FIG. 9.—Per cent free and bound water content of Granary Weevils.

other words, "the chain is no stronger than its weakest link." Many species have not yet reached the outer boundary of their migration; and it seems possible, by studying the correlation between low temperatures on the one hand and water binding and water holding capacity of colloids on the other, to place a limit upon the spread of any given species which is exposed during some stage of its development to the low temperatures of winter.

SUMMARY

Some previous evidence is given for the existence of bound water in a hydrophilic colloid system, and for adsorption of water being directly proportionate to winter hardiness of plants.

[14] Chapman, R. N., "Animal ecology with especial reference to insects." Minneapolis, 1925.

The present series of experiments was conducted to determine if the phenomenon of adsorption of water under low temperatures observed by Newton[10] for wheat plants would hold for insects.

The heat-of-fusion method of Thoenes[13] for separating free and bound water was used, and detailed description of the method and its application is given.

The insects used comprised a hardy, a neutral and a non-hardy species; and it was found as the experiments progressed that the different species gained or lost in bound water in direct proportion to their winter hardiness.

The biological significance and the advantages to the species of having the free water transformed into the bound form upon the approach of winter is discussed.

Acknowledgment

I am much indebted to Dr. R. A. Gortner, Chief of the Division of Biochemistry of the University of Minnesota, who first suggested to me this subject of the possible relationship between hydrophilic colloids and cold resistance of insects. My thanks are also due to him for placing at my disposal much of the data in connection with adsorption phenomena which I have incorporated into this paper; and for his assistance and advice as the present series of experiments were being conducted.

University of Minnesota Agricultural Experimental Station,
St. Paul, Minnesota.

COLLOID TYPES

By Eugene C. Bingham

Within certain defined limits the shearing of true fluids takes place in direct ratio to the shearing stress.[1] On the other hand solid substances, no matter how much they may differ from each other in most respects, have this in common that they are not continuously deformed in direct ratio to the shearing stresses.[2] It is in fact this characteristic, this so-called "break-down" of Poiseuille's Law, which sharply demarcates the flow of solids and is spoken of as "Plastic Flow."

The use of the word "continuously" is made necessary by the fact that elastic deformation, as expressed by Hooke's Law, takes place in direct ratio to the shearing stress; but the deformation is instantaneous and not proportional to the *time* that the shearing stress acts as in viscous and plastic flow.

Non-Polar Colloids

Since instantaneous elasticity[3] is just as properly a property of viscous liquids as of plastic solids, a very fundamental classification of solids is the one based upon our conceptions of flow. At first it was not recognized that there are quite distinct types of plastic flow but we must certainly recognize three types and there may be others.

A suspension of a finely-divided solid in a very viscous medium affords an example of one type.[4] Assuming the yield value to be the shearing stress required to start the continuous deformation, the amount of deformation has been found to be directly proportional to the excess of shearing stress, i.e.,

$$v = \mu(F - f)r, \qquad (1)$$

the mobility μ being the analog of the fluidity.

At Lafayette College[4] we have used three different types of instruments for testing the validity of the above equation. 1. The variable pressure viscometer,[5] with its constant volume of efflux is precise but it is limited by the necessity of reading the meniscus. 2. In the first form of the plastometer,[6] the material was extruded and weighed, and

[1] Bingham, "Fluidity and Plasticity," McGraw Hill Book Co., pp. 1-80 (1922).
[2] *Ann. Phys.*, (4), 19, 985 (1906).
[3] *J. Franklin Inst.*, 197, 99 (1924).
[4] Bingham, Bruce and Wolbach, *J. Franklin Inst.*, 195, 303 (1923).
[5] *U. S. Bureau Standards Bull.* 14, 59 (1917) (Scientific Paper No. 298); *J. Ind. Eng. Chem.*, 6, 233 (1914); *Proc. Am. Soc. Testing Materials*, 18, II (1918).
[6] *U. S. Bureau Standards Bull.* 13, 309 (1916) (Scientific Paper No. 278).

with this also the pressure was varied. 3. In the newer penetration method,[7] the pressure is kept constant and the varying shearing stresses calculated for the different distances that the material penetrates the capillary. Each form of instrument has its advantages as well as disadvantages, but the combined use of several widely different instruments is of unquestioned advantage for the possibility of disagreement in the methods was early pointed out.[8] It is all the more important to avoid uncertainties in regard to our plasticity constants because of difficulties which are inherent in the materials studied. Solids are not reproducible as fluids are. The crystalline structure, the size of the particles, traces of deflocculants, imprisoned air or moisture, the age and the amount of shearing given to the sample are factors of importance outside of the plastometer. Keeping all of the factors as nearly as possible constant except the one which is the object of study, some progress has already been made in controlling these factors.[9] The work of G. Raymond Hood, Herrick R. Arnold, Paul R. Nelson, and Vinton R. Rawson has demonstrated that for suspensions in a viscous dispersion medium there is fair agreement between all three types of instruments studied thus far.[10] The corrections for the different instruments have, however, not yet been fully evaluated hence instruments should still be compared over the same general range of shearing stresses.

The best results are obtained for this type of colloid when the fluidity of the dispersion medium is quite low, as in paints. Clay suspensions in water have proved difficult to measure and the flow-shearing stress curves are not satisfactorily linear. Buckingham[11] tried to account for this on the basis of slippage and this is probably the most promising line of attack. At any rate, according to German,[12] no method of logarithmic plotting has proved useful with this type of flow, which seems to be in direct contrast to that next to be considered.

Before leaving this type, it may be stated that the effects upon the plasticity of changes in temperature, fluidity of the medium, concentration of the disperse phase, size of particle and the presence of deflocculating agents are fairly well known.[13]

Emulsions

Fats and greases resemble most nearly Type 1. The molten fat behaves like a viscous liquid, but as soon as solidification begins the

[7] Bingham and Murray, *Proc. Am. Soc. Testing Materials*, 23, II, 655 (1923).
[8] *Ibid.*, page 662.
[9] Bingham and Green, *Proc. Am. Soc. Testing Materials*, 19, II, 640 (1919).
[10] Thesis of Lafayette College, data unpublished.
[11] *Proc. Am. Soc. Testing Materials*, 21, II, 1154 (1921).
[12] Thesis of Lafayette College.
[13] *Cf.* Bingham and Jacques, *Ind. Eng. Chem.*, 15, 1083 (1923).

material is plastic, and remains plastic as long as the liquid phase is present, e.g. down to the eutectic. The yield value according to the measurements of Brownmiller and Wiggins [14] increases steadily as the temperature is lowered (Fig. 1) and the mobility decreases (Fig. 2). At temperatures below the eutectic, deformation must result from shearing of one or more of the solid substances so that the curves show a discontinuity at the temperature of complete solidification.

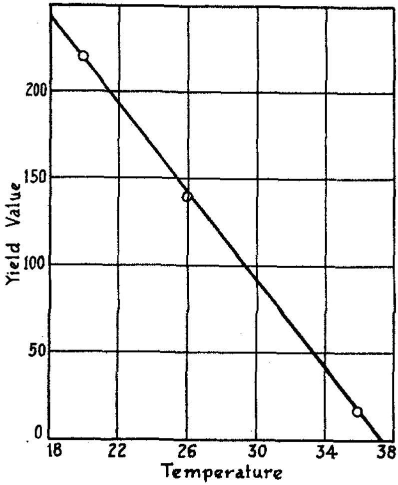


FIG. 1.

POLAR COLLOIDS

Polar colloids of the gelatin-in-water type certainly do not follow equation (1) and the difference seems to be not one of degree but to constitute a different class entirely. In Figure 3 Curve *A* there is given as an example a 1.71 per cent solution of nitrocellulose in dibutylphthalate from measurements of Samuel Ellis.[14] The reciprocal of the time of flow of 4 ml. of the solution in viscometer number is plotted against the shearing stress in dynes per square centimeter. The curve does not approach linearity at any shearing stress and it passes

[14] Thesis of Lafayette College.

through the origin at a finite slope. Various logarithmic formulas have been suggested for this type of flow such as $v = a F^n$ by Wo. Ostwald[15] and $v = a (F - f)^n$ by W. Herschel.[16] Neither of these equations, however, passes through the origin at a finite slope. An equation which has

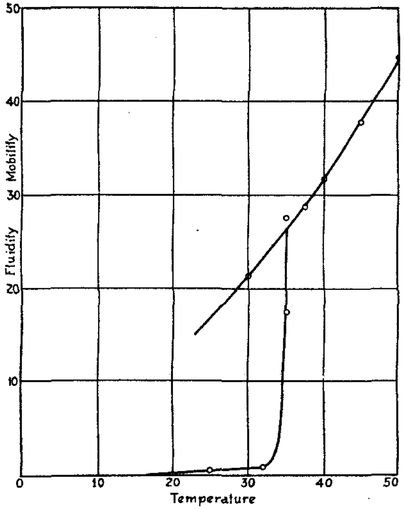


FIG. 2.

these properties, which seem to be characteristic of many colloidal solutions of this type, has been suggested by Dr. F. Williamson[17] as

$$v = a F + b F^n \quad (2)$$

and in a study of nitrocellulose solutions he found the value of n to be almost exactly 2.

Since v/F is proportional to the apparent fluidity Φ_a we may write the equation as

$$\Phi_a = \alpha + \beta F \quad (3)$$

where α and β are constants. The former may be interpreted as the fluidity of the material at zero shearing stress and may be dependent

[15] *Kolloid-Z.*, 36, 99, 157 (1925).
[16] *Ind. Eng. Chem.*, 16, 927 (1924).
[17] Privately communicated from E. I. du Pont de Nemours and Co.

upon the viscous flow of the medium through the micellian structure. That the equation (3) does give satisfactory results for nitrocellulose solutions, the data of Figure 3 are replotted in Figure 4, using apparent fluidities as ordinates. At the same time the logarithmic plotting given in Curve *B* in Figure 3 shows the great superiority of the Williamson curve for this particular type of solutions. Were the solution a true fluid, the apparent fluidity would be independent of the shearing

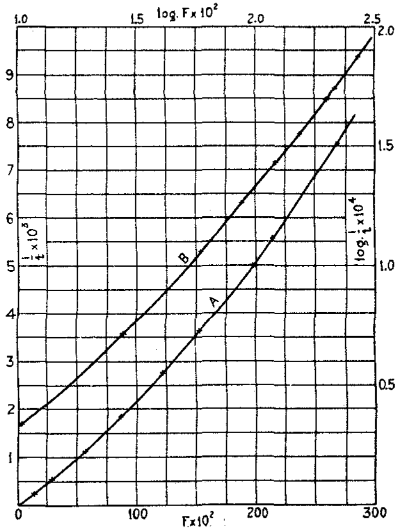


FIG. 3.—Shearing stress in dynes per cm².

stress, but it actually increases as a linear function of the shearing stress. If the solution were a true fluid the Curve *A* in Figure 3 would be linear so that the constant β seems to be particularly characteristic of that property which gives the material the properties differentiating it from a true liquid. The parameters α and β appear to be independent of the dimensions of the instrument used in their determination. Mr. Wiggam[18] has found the equation to apply to solutions in some ten solvents of as many types of nitrocellulose.

[18] Privately communicated from Hercules Powder Co. Experimental Station.

The results of increase in concentration of the disperse phase or of change in temperature is far more pronounced in the case of polar colloids than in the non-polar type. The so-called "solubility" of polar colloids has long been roughly measured by the apparent viscosity of the solution in different "solvents." This method is of course open to various objections for we are not here dealing with true solutions nor true viscosities and if we were, it is not apparent that the one would be a direcet measure of the other.

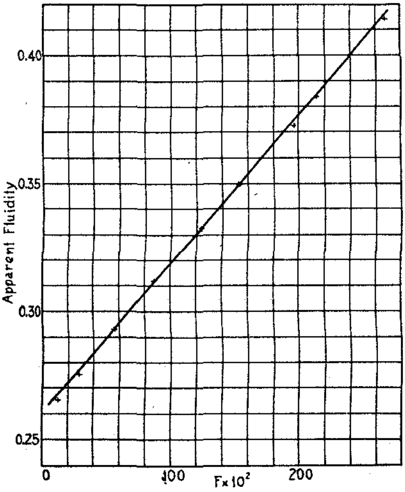


FIG. 4.

If there is a concentration at which the colloidal dispersion just behaves like a true fluid, then that concentration might be regarded as most nearly analogous to a true solubility. However, it seems likely that colloidal solutions of the type we are here considering do not become true fluids except at very low concentrations indeed. It, therefore, seems most logical to compare the values of β at similar concentrations in different solvents. Obviously that solution is most nearly a true fluid in which β is the smallest.

As a colloidal solution is warmed, the curve obtained by plotting the rate of flow against the shearing stress becomes more and more

nearly linear or β becomes smaller and smaller. When the curve is linear and β is equal to zero, the material becomes a true fluid and the temperature is the analog of a melting temperature or rather of the temperature of complete solution.

There are two other methods for estimating the relative solubility of colloids which may be mentioned. One depends upon the measurement of the amount of so-called "non-solvent" required to start the

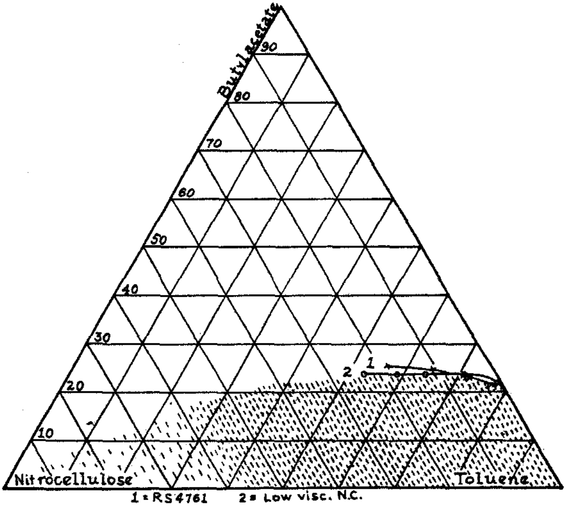


FIG. 5.—Mutual solubility relations between nitrocellulose, butyl acetate and toluene by M. C. Moore using precipitation method.

precipitation of the colloid. Figure 5 shows the results of some measurements made by Malcolm C. Moore[19] of the Hercules Powder Company, using two varieties of nitrocellulose dispersed in butyl acetate with toluene added to produce inhomogeneity. Sample 1 differs from sample 2 in having a much higher viscosity. All of the mixtures in the shaded area are inhomogeneous while the light area represents complete dispersion. The end-points are sharp so long as the dispersions are free flowing but the curves could not easily be extended beyond the

[19] Privately communicated from Hercules Powder Co. Experimental Station.

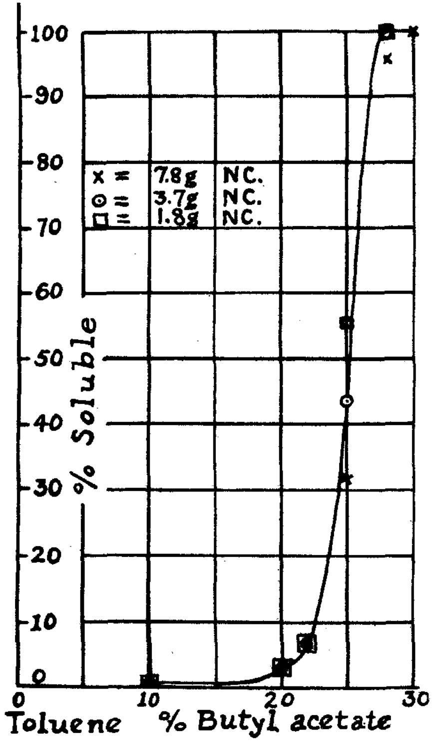


FIG. 6.—Percentages of nitrocellulose dissolved in 100 grams of solvent containing butyl acetate and toluene, using different weights of nitrocellulose, by M. C. Moore.

points given. It appears possible that nitrocellulose and butyl acetate are miscible in all proportions. Nitrocellulose and toluene seem to be mutually insoluble. Very small percentages of nitrocellulose are sufficient to render butyl acetate and toluene immiscible. This diagram suggests the application of the phase rule to colloidal solutions. The

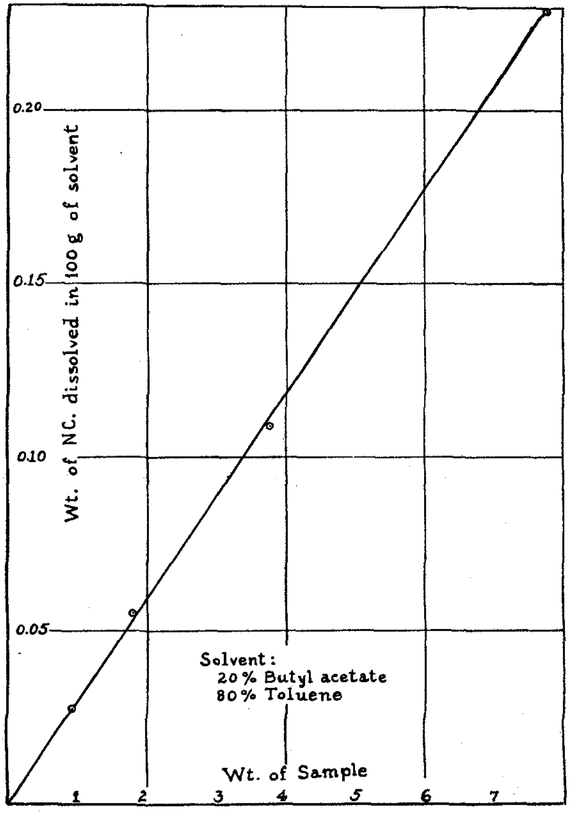


FIG. 7.—Ratio of weight of nitrocellulose dissolved in 100 grams of solvent to weight of sample in solvent mixture of 20 per cent butyl acetate and 80 per cent toluene. By M. C. Moore.

same sort of a diagram applies equally well to the case where two of the components are colloids. Such colloids which are immiscible in each other are gelatin and agar, or rubber and nitrocellulose, etc.

The second method is the solubility method. Moore has shown that in 100 grams of solvent mixture, the concentration of butyl acetate in the solvent, necessary for complete solution, is nearly independent of the weight of the sample of nitrocellulose, as shown in Figure 6. The results may be expressed in another way by stating that the weight of nitrocellulose dissolved in 100 grams of solvent is directly proportional to the weight of the sample. This is true over quite a range of concentration but the end-point is not as easy to determine as in the first method (Fig. 7).

Applying these methods to various solvents would reveal their solvent ability, but more than one non-solvent should be employed since a given non-solvent may not be inert and it may interact with one solvent more than another.

As the amount of nitrocellulose is increased, the ratio of the amounts going into the two phases remains constant, but as the percentage of butyl acetate in the mixture is increased the ratio approaches unity, which is the value on the curves of Figure 5.

The Flow of Crystalline Substances

The flow of a single crystal takes place along slip planes and is entirely different from the types of flow already considered in that respect. Ordinary crystalline material would appear to present a more complicated case of flow, but the data of Trouton and Rankine [20] on the flow of lead wire indicate that the flow, after it becomes fully established, is a linear function of the time. At low shearing stresses, the deformation is nearly but not quite in accordance with Hooke's Law.

In the study of colloid types described above it may be noted that the property of length or shortness may be found in every kind of plastic substance, such as dough, glue, paint, steel, etc. The comparative suddenness with which flow begins in a plastic solid of high mobility as soon as the yield value is exceeded, makes it easy to get a mental picture of these properties.

Lafayette College,
Easton, Pa.

[20] *Phil. Mag.* (6), 8, 538 (1904).

THE CONSISTENCY OF CASEIN GLUE

BY F. L. BROWNE[1] AND DON BROUSE[2]

SUMMARY

1. The consistency relations of casein glue are of special significance in the study of the technic of gluing operations and in the investigation of factors governing the permanence of water-resistant casein glues under damp conditions of service.

2. Measurement of the consistency of casein glue in absolute units, including the determination of flow-pressure diagrams, is seriously complicated by the facts that (*a*) the consistency often changes with time fairly rapidly, (*b*) different batches of glue made up as nearly as possible in the same way do not agree exactly in their consistency relations, and (*c*) it is difficult to establish a satisfactory datum point during the preparation of a casein glue from which to begin counting the working life.

3. The use of a modified form of the Herschel consistometer is described and some of its drawbacks for observations upon casein glue are pointed out.

4. Flow-pressure diagrams for solutions of casein containing no calcium hydroxide indicate that they have more complex flow characteristics than the lime-containing, jelly-forming glues, which appear in the light of the evidence thus far obtained to be truly viscous.

5. The flow-pressure diagrams for jelly-forming water-resistant casein glues (containing lime) fail to reveal any transition from viscosity to plasticity with lapse of time after mixing, at least until the consistency has passed far beyond the condition ordinarily considered "set." Neither does the viscosity-time curve exhibit any sharp break. The "setting" point must therefore continue to be defined arbitrarily; but the use of the viscosity-time curve permits cancellation of the personal factor. It is suggested that the glue be considered "set" when the viscosity reaches 1000 poises.

6. Illustrations are given of the change in viscosity of water-resistant casein glues with (*a*) time, (*b*) alkalinity, and (*c*) water content, and the practical significance of these relations is briefly discussed.

[1] Chemist in Forest Products, U. S. Forest Products Laboratory, Madison, Wis.
[2] Assistant Engineer in Forest Products, U. S. Forest Products Laboratory, Madison, Wis.

Introduction

Consistency studies of casein glue are significant to the woodworker in two connections. In the first place, since the fundamental principle underlying the production of strong joints in gluing wood, given a suitable woodworking glue, is the reciprocal relationship between pressure and glue consistency at the time of applying pressure,[3] the investigation of factors influencing gluing operations can often be resolved into a laboratory measurement of their effect on consistency without resort to the difficult and tedious technic of joint strength tests. In the second place, consistency is a conveniently measurable physical property which is extremely sensitive to changes taking place in the chemical composition or colloidal state of the glue itself. It is believed that a study of the rate of change in the consistency during the working life of casein glues of different kinds will throw much light on the very important but hitherto inadequately studied property of the *permanence* of water-resistant casein glues under prolonged exposure to damp conditions. Glues which are highly water resistant when first prepared do not necessarily remain so after they have been subjected to moisture for some time.

Heretofore most investigators of the consistency relations of glues[4] have been content to choose conditions of concentration and temperature suitable for the viscometers conveniently available rather than to develop instruments capable of operating with glues in the state in which they exist on the glue spreader or in glue joints at the time of applying pressure. Even in the standard method for grading animal glues[5] such deference to expediency has been noted. However, for the purposes of the present study it was essential to deal with glues as they are used in the glue room, and apparatus was therefore required capable of handling very viscous fluids and of detecting and measuring, as accurately as conditions would allow, departures from simple viscous flow. It was also considered desirable that the instrument should give results in terms of absolute units of viscosity.

Apparatus and Procedure

The instrument employed, Figure 1, is a modification of the original type of Herschel consistometer[6] developed for measuring the consistency of paints and varnishes. The changes in design are minor in character. The brass castings are lightened in order to reduce the heat capacity

[3] Browne and Truax, "Colloid Symposium Monograph," Vol. IV, p. 262 (1926).
[4] For a review of the literature on consistency of glue see Bogue, "The Chemistry and Technology of Gelatin and Glue." McGraw-Hill, 1922, p. 186.
[5] De Beukelaer, Powell, and Bahlman, *Ind. Eng. Chem.*, 16, 310 (1924).
[6] *See* Gardner and Holdt, *American Paint and Varnish Manufacturers Association Cir. No.* 127. Herschel has also modified the original design of his instrument; see *Oil Gas J.*, 25, 146 (1926).

and facilitate rapid adjustment to the temperature of the water thermostat. Container *A*, in which the glue is placed for test, is much longer than in Herschel's original model so as to accommodate a larger sample. The connecting section *B* is shortened to let the tip of the brass capillary *D* extend into the glass collecting vessel *C*, thus permitting observation of the glue while it is being extruded from the capillary. The glass collecting vessel fits snugly into a rubber stopper closing the lower end of *B*, where it is held in place firmly by a brass swing and wing bolt as shown instead of screwing into a threaded stopper. The brass capillary passes freely through the rubber stopper so that at the proper time its end may be exposed to back-pressure of air admitted through the opening *H*. The figure indicates that *C* is made of a short piece of glass tubing with its end closed by a rubber stopper. That device proved fairly satisfactory but has been replaced by a short glass test tube, 2 x 7.5 cm. Several interchangeable capillaries are provided for use with glues of widely differing consistencies. The insertion of the tap *F* in the top of the container *A* through which a thermometer can be introduced into the glue, completes the alterations made in Herschel's original design of the instrument.

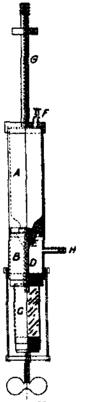


FIG. 1.—The modified Herschel consistometer.

Auxiliary apparatus for use with the consistometer include a water thermostat, a source of compressed air at controlled pressures, and a mercury manometer. The compressed air is obtained by means of a small compressor supplying a storage tank of a little over 4 cubic feet capacity. Before a run the pressure in the tank is built up to about 60 pounds per square inch and the compressor shut off. Air is drawn off into the supply line through an adjustable pressure-reducing valve which is set at a point giving the desired pressure. The pressure as measured with the manometer is found to vary less than 1 mm. of mercury during the course of a consistency measurement. As the measurements are made within a pressure range of 80 to 650 mm., the degree of precision afforded is far within the limits of experimental error fixed by the reproducibility of the glues themselves.

To carry out a consistency measurement, the vessel *C* is weighed and the consistometer assembled except for the cover of container *A*. Outlet *H* is attached to a rubber tube communicating through a 3-way stop-cock with the air supply line. By applying back pressure at *H* judiciously, controlling it roughly by means of the stop-cock, the capillary can be effectively blocked so that container *A* can be filled with either a viscous or a plastic material without any of it flowing through

the capillary. The cover of container A is now screwed in place and the instrument submerged in the water bath. When the desired temperature has been attained, the tube G is attached to the air supply through another 3-way stop-cock set in the closed position. All being in readiness, outlet H is opened to the atmosphere, preventing development of back pressure during extrusion, and pressure is applied through tube G. The end of the capillary is then observed by looking through a window provided in the side of the thermostat, and as soon as material appears at the end of the capillary a stop-watch is set running. During the extrusion the pressure indicated by the manometer is recorded. When a suitable amount [7] of material has been received in the vessel C, outlet H is connected to the air pressure by turning its stop-cock just after a drop of material has fallen from the end of the capillary and the stop-watch is arrested at the same instant. Before another drop has fallen from the capillary, the other stop-cock is turned to connect tube G to the atmosphere, whereupon any additional material that may have gathered at the end of the capillary in the meanwhile is forced back into A. The apparatus is then removed from the thermostat and vessel C is disconnected, dried, and weighed, the increase in weight representing the mass of material extruded in the measured time under the recorded pressure.

The temperature at which all measurements discussed in this paper were made is 25° C.

The pressure effective in the extrusion of the material is the recorded pressure plus the average hydrostatic head of the material during the measurement, which is calculated by the method of *Bureau of Standards Technological Paper* No. 210. The capillary tubes were calibrated with the aid of glycerine-water solutions, the viscosities of which are given in *Bureau of Standards Technological Paper* No. 112. For methods of calculating viscosities and consistencies see Herschel, chapter 45 of "Colloid Chemistry," edited by Alexander.

Dr. Herschel points out in a private communication that calculation of the correction for hydrostatic head of the material in the container is beset with some uncertainty when dealing with very viscous materials because it may not be correct to assume that the resistance to flow is negligible outside of the capillary, and the hydrostatic head might be balanced, more or less, by this resistance to flow in the container. Moreover, with plastic materials the method of calculation of *Technological Paper* No. 210 is not strictly applicable because it assumes that the material obeys Poiseuille's law. As a matter of fact, the correction for hydrostatic head in the studies thus far has been much smaller than other uncertainties due to experimental difficulties. In future work no attempt will be made to correct the pressure as read on the manometer for hydrostatic head of material in the container.

[7] This amount is usually so regulated as to cause a change in level of 1 cm. in the container A.

Typical Results with Casein Glue

Composition of Casein Glue.—The composition of casein glue, that is, its formulation, has been discussed by Browne.[8] This view, briefly stated, is that any aqueous solution of casein of appropriate consistency and sufficiently high concentration with respect to casein may be used as a glue. Within what limits the consistency is appropriate and the concentration sufficient, however, cannot be stated with precision or even with rough approximation at the present time. Industry has been guided in such matters thus far by craftsmanship, not by technology. But by way of illustration it may be said that glues used in American wood-working practice may contain 2 or 3 grams of water per gram of casein and may have a viscosity (or an apparent viscosity under 350 gm. per square cm. pressure) of 50 to 200 poises. In Europe two or three times as much water per gram of casein might be employed, keeping the consistency in somewhat the same general region by control of the alkalinity.

Some colloid chemists will question the propriety of the word "solution" in this rather clumsy effort to define a casein glue. The writers are merely following common parlance and imply nothing more than a disappearance of the outlines of most of the individual granules of casein to form what appears to the unaided eye to be a reasonably homogeneous preparation.

Casein glues can be made by dissolving casein in water that has been rendered sufficiently alkaline with sodium or ammonium hydroxide, a hydrolyzable salt such as borax or tri-sodium phosphate, or a mixture of reactants producing sodium hydroxide, say calcium hydroxide and sodium fluoride. Such adhesives remain in a suitable range of consistency for a relatively long time, gradually becoming more fluid as the casein hydrolyzes or decomposes by microbiological action. They are not water resistant and find little or no use in woodworking. If, however, an excess of calcium hydroxide is added, the behavior is radically altered. The viscosity of the freshly prepared solution increases—slowly at first, then more rapidly, until the consistency passes out of the range suitable for application by the customary glue room machinery and the glue is said to have reached the end of its "working life." After passing through that indefinite stage in which it is difficult to say whether it is a sol or a gel, it becomes a clearly defined jelly possessing elasticity measured usually in terms of "jelly strength." Such glues are water resistant, some of them more so than others.

Consistency of Casein Solutions Containing No Lime.—Many investigators[9] have studied the viscosity of dilute solutions of casein.

[8] Sutermeister, "Casein and Its Industrial Applications," chapter 7. Chemical Catalog Co., 1927.

[9] *See for example* Loeb, *J. Gen. Physiol.*, 3, 547 (1921).

Zoller,[10] who alone seems to have approached the subject from the point of view of its application to casein glue, found that increasing the concentration with respect to casein to 9 per cent gave results that could not be predicted on the basis of previous studies with more dilute solutions. Zoller's solutions, because of the limitations of his apparatus, were still far more dilute than those used as glues. More-

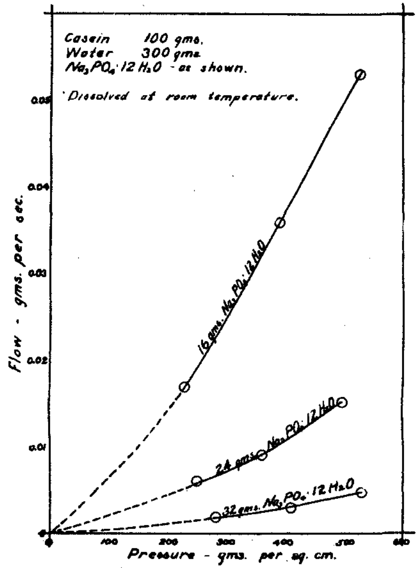


FIG. 2.—Flow-pressure diagram of a mixture of casein and tri-sodium phosphate.

over, he worked with mixtures contining no calcium hydroxide and in a region of pH far removed from that characteristic of American water-resistant glues. He also seems to have neglected to determine whether his solutions were truly viscous or exhibited a more complicated type of flow.

Solutions of casein containing no calcium hydroxide were used in

[10] *J. Gen. Physiol.*, 3, 635 (1921).

our first experiments both for the purpose of establishing continuity with Zoller's work and because it was presumed that such solutions, lacking the tendency toward gelation, would exhibit relatively simple flow characteristics. Figure 2 shows typical flow-pressure diagrams for three solutions of casein in tri-sodium phosphate. The casein employed in these and all other mixtures to be described here was taken from a single shipment of commercial casein imported from Argentina

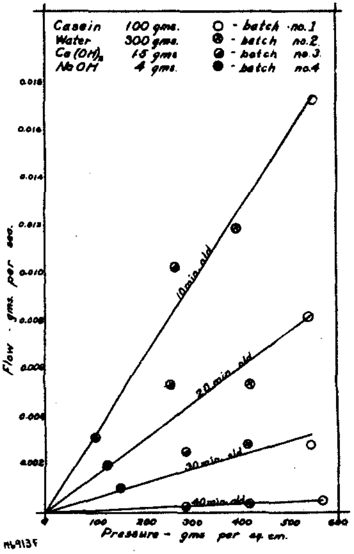


FIG. 3.—Flow-pressure diagram for a water-resistant casein glue of low alkalinity.

and presumed to be of the "natural-soured" type. The solutions were prepared by dissolving respectively 16, 24, and 32 grams of crystalline tri-sodium phosphate in 400 grams of water at room temperature, stirring in 100 grams of casein, and allowing the mixtures to stand over night for the casein to dissolve.

The flow-pressure diagrams are not straight lines passing through the origin, according to Poiseuille's formula, characteristic of ideally viscous fluids, but exhibit the complex relationship found in such sols

as rubber-benzene solutions and solutions of nitrocellulose.[11] The consistency of casein-phosphate solutions falls off extraordinarily as time passes, until they become almost as mobile as water after a few days. If the solutions are heated during preparation in order to hasten solution and are then cooled, much higher consistencies are observed than those in the corresponding cold-prepared solutions, but the flow-pressure dia-

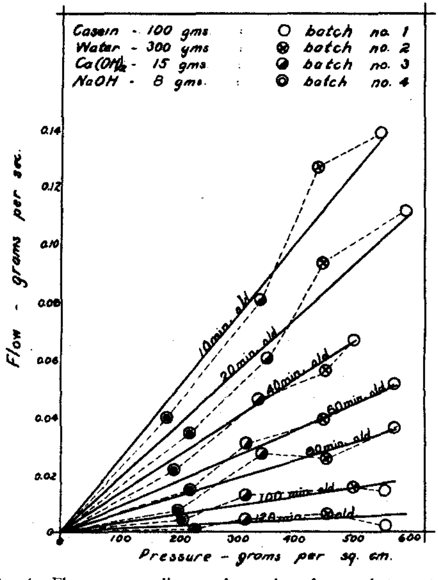


FIG. 4.—Flow-pressure diagram for a glue of somewhat greater alkalinity than that of Fig. 3.

grams are still curved. Similarly complex relationships were observed in solutions of casein in borax. It became obvious that, unless a long and laborious research was carried out, the study of these "simple" casein solutions could neither serve to establish contact with Zoller's work nor afford an easy approach to the investigation of the more important lime-containing glues.

[11] *See* Bingham, "Colloid Symposium Monograph," Vol. II, p. 106 (1924).

Consistency of Lime-containing Casein Glues.—Flow-pressure diagrams for two jelly-forming, water resistant casein glues having working lives of about 35 to 120 minutes respectively are shown in Figures 3 and 4. The glues were made by soaking 100 grams of casein in 200 grams of water at 25° C. for a few minutes and then stirring in a solution of 4 or 8 grams of sodium hydroxide in 100 grams of water containing 15 grams of calcium hydroxide in suspension. The mixing was done in a suitable motor-driven mixer and was continued for 5 minutes. The batches were then allowed to stand 5 minutes, when they appeared properly dissolved and the working life was arbitrarily assumed to begin. Obviously that moment cannot be determined with great precision.

With a single consistometer of the Herschel type it is manifestly impossible to carry out measurements of the same glue batch under different pressures at the same instant of time. The process of extrusion of a suitable amount of material through the capillary alone may take as long as 3 minutes, to say nothing of the time needed to prepare for a second extrusion under different pressure. But the consistency is changing rapidly with time, going in the case of the glue of Figure 3 from an initial viscosity of 190 poises to more than 1000 poises in the course of half an hour. To obtain the data for Figures 3 and 4 it was therefore necessary to use successively 4 different batches of each glue and to run each batch under a particular fixed pressure at several time intervals during the working life. When due consideration is given to the rapid change in consistency during the time of measurement, to the necessity for using different batches of glue for each pressure, to the fact that different batches prepared as nearly as possible in the same way do not agree precisely in consistency, and to the difficulty of establishing a satisfactory datum point for the beginning of the working life, it will be appreciated that the consistometer described cannot be expected to differentiate with certainty between viscous and plastic flow in casein glue. An instrument with which measurements of flow under several different pressures could be made simultaneously on the same batch of glue would be highly desirable.

In view of the difficult experimental conditions, the indications of the data in Figures 3 and 4 are probably as consistent as can be expected. The only reasonable interpretation that can be placed upon the curves is that the glues are either truly viscous or very nearly so throughout the period of the working life and even beyond, since the last curve of Figure 3 represents a condition well past the point at which the glue is usually considered "set," while the last curve of Figure 4 coincides very closely with that condition. The fact that such glues turn out to be viscous rather than plastic constitutes a helpful simplification of the problem of routine use of consistency measurements in the study of casein glues, because viscosity can be determined by a single flow

measurement under any convenient pressure. It still remains to be seen, of course, whether all commercially important casein glues are typified by the ones studied thus far.

Further evidence of the viscous character of casein glues of this type is furnished by the flow-pressure diagram, Figure 5, all of the

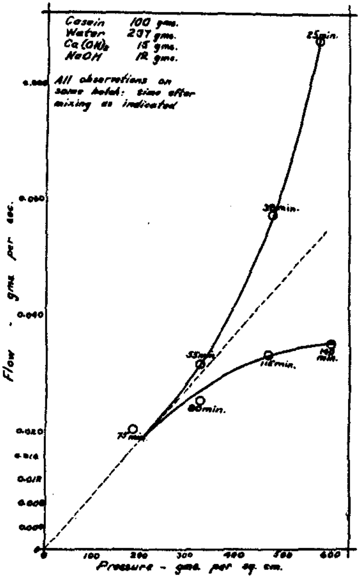


FIG. 5.—Flow-pressure diagram for a glue of rather high alkalinity (all observations made on the same batch of glue).

data for which were obtained with a single batch of glue. The glue was somewhat more strongly alkaline than the one used for Figure 4, containing 12 grams of sodium hydroxide per 100 grams of casein, and therefore having a much longer working life. The time after mixing at which the determinations were made is indicated by the figures adjacent to each point. The first determination was made at the highest pressure, and successive measurements at lower pressures, then further observations were noted with stepwise increase in pressure again, all

time intervals being approximately equal. As would be expected, supposing the glue truly viscous and the viscosity increasing with time, the line joining the points observed with decreasing pressures is concave upward, that obtained with rising pressures concave downward. Presumably the straight line joining the origin with the cusp of the

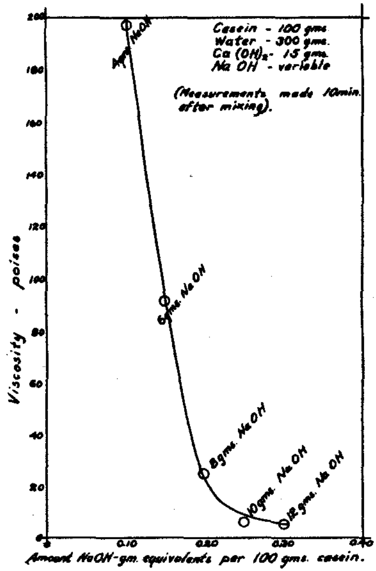


FIG. 6.—The relation between viscosity and alkalinity for a typical family of water-resistant casein glues.

curves is an approximate representation of the flow-pressure relations of the glue when it is about 75 minutes old.

The Change in Viscosity with Time.—Figure 6 shows the relationship between viscosity, calculated by Poiseuille's formula as for truly viscous substances, and time after mixing for five lime-containing glues of widely varying working life. The data from which each curve was plotted were obtained with a single batch of glue. Apparently the curves all belong to the same family, although the scale of

abscissas varies enormously. The viscosity increases relatively slowly during the early part of the working life. At a period closely identified with the end of the working life as usually estimated, the curve bends sharply as the viscosity begins to increase very rapidly. But throughout the region investigated the viscosity-time curve is smooth and exhibits no sharp break which might serve as a definite limit for the working life to replace the arbitrary personal judgment with which investigators have been content heretofore. The flow-pressure diagrams, Figures 3 and 4, likewise fail to reveal any point of transition from viscous to plastic flow. The transition from sol to gel must, then, lie well beyond the condition which is practically defined as "set." However, the use of the viscosity-time curve for describing glue consistency at least permits of cancelling the personal factor by adopting some arbitrary limit of viscosity for the end of the working life. If the glue is considered "set" when the viscosity reaches 1000 poises, the working life thus defined will be of the same order of magnitude as the values to which we have become accustomed in the past.

The shape of the viscosity-time curve is of practical significance in the glue room. During the time that the glue is on the spreader it is highly desirable that the viscosity remain reasonably constant to facilitate obtaining uniform spread of glue with a minimum amount of attention to the adjustment of the machine. The rapid increase in viscosity taking place near the end of the working life and subsequently is probably an indication that the internal transformations within the glue by which the jelly becomes irreversible take place promptly in the glued up stock. Presumably the spontaneous gelation without dehydration of lime-containing casein glues is identical with or at least intimately associated with that quality of such glues which gives them the desirable feature of water resistance.

The Influence of Alkalinity on Consistency.—The important influence of the alkalinity [12] of the glue on its viscosity is apparent in Figures 6 and 8 and on comparing Figures 3 and 4. It is further emphasized by Figure 7. Over a fairly wide region of high ratios of sodium hydroxide to casein the viscosity is relatively independent of the alkalinity, but when the proportion of sodium hydroxide is decreased beyond a certain point the viscosity increases rapidly. In other words, a weakly alkaline glue of suitable viscosity for woodworking contains more water and is therefore relatively cheaper, if applied with the same thickness of wet glue line, than a strongly alkaline glue. How far it is safe to go with dilution of the glue through control of the alkalinity before there is danger of obtaining weak joints has not yet been determined. American practice has been confined practically to

[12] It would be more significant to express the alkalinity in terms of pH, but measurements of hydrogen-ion concentration in viscous glues require a preliminary investigation of the reliability of the methods customarily employed for less viscous and more dilute solutions. Such a study is in progress and will probably be the subject of a future publication.

the region of high alkalinity, largely because such glues have a relatively long working life. Weakly alkaline glues containing much calcium hydroxide "set" quickly, as Figure 6 shows.

The Influence of Concentration on Viscosity.—Figure 8 is typical of the viscosity-water content relation for casein glues. In order that the observations (which were of necessity made of different batches) might be as fairly comparable as possible, the readings were taken 10 minutes after the beginning of the mixing operation.

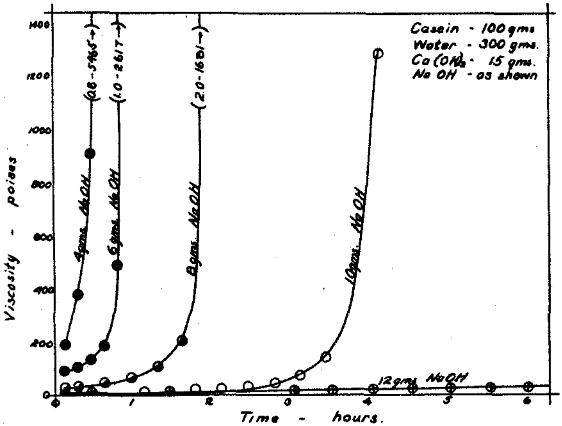


FIG. 7.—The relation between viscosity and time for a typical family of casein glues.

The powerful influence of water content on the viscosity of the mixture may be one of the reasons why exact duplication of glue batches with respect to viscosity is difficult, for it is not easy to control the amount of water in a glue solution with a high degree of precision. The high rate of increase in viscosity with diminishng water content shown by Figure 8 has an important practical bearing which does not seem to be fully appreciated by all makers and users of casein glue. It has been shown[13] that, in the freshly assembled glue joint, water is rapidly abstracted from the glue line as a result of absorption by the wood. The nature of the concentration-viscosity curves of Figure 8 makes it clear why casein glue "sets" so much more rapidly in

[13] Browne and Truax, "Colloid Symposium," Vol. IV, p. 261 (1926).

the assembled joint than it does by spantaneous gelation without dehydration. Commercial glues may have a working life of 8 hours or more and yet wood joints (in parallel-grained gluing) are strong enough within less than one-half hour after pressing to be removed from the

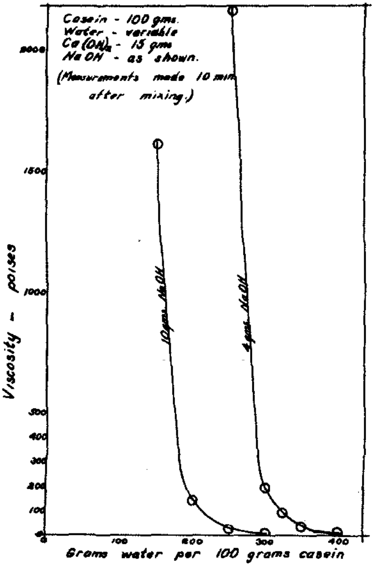


FIG. 8.—The relation between viscosity and water content for two casein glues differing in alkalinity.

press, and within 4 hours they are strong enough to be machined. Of course, it is not common practice in woodworking plants to remove joints from pressure for machining so soon after assembling, because it is not often advantageous; and furthermore it is good practice to allow a large factor of safety in factory operations of that kind.

U. S. Forest Products Laboratory,
Madison, Wisconsin.

PLASTICITY AND SOLVATION OF CELLULOSE ESTERS[1]

BY S. E. SHEPPARD, E. K. CARVER AND R. C. HOUCK.

The reason why some substances are better solvents for cellulose esters than others, and especially why mixtures of solvents are so often better than the pure solvents, has always been a subject of speculation.

Some of these theories are based on the idea that one or the other of the solvents is the one which is peptizing the ester, and that the improvement in solvent power on the addition of another solvent, is due solely to its action in changing the molecular association of the first solvent. Such are the theories of Barr and Bircumshaw[2] and of Byron.[3] One of these theories assumes that polymerized alcohol is the solvent for nitro-cellulose and that addition of ether increases the polymerization, while the other theory assumes that dissociated alcohol is the solvent, and that addition of ether increases the dissociated alcohol. Obviously, both of these theories cannot be correct. Moreover, these theories have the disadvantage of being too specific. There are many mixtures of liquids which are better solvents for cellulose esters than either of the liquids pure, in which there is no particular evidence of polymerization. It appears that any theory which is to be satisfactory must be general enough to apply to all cases.

Another theory which appears much better but which also is somewhat too specific is that proposed by Esselen.[4] His theory explains the fact that cellulose acetate is dissolved better by a mixture of alcohol and chloroform than by chloroform itself.

He assumes that the cellulose acetate which is known to have considerable attraction for hydroxyl groups, adsorbs the alcohol with the hydroxyl group inside. This leaves the acetate molecule covered with ethyl groups and these ethyl groups tend to dissolve in the chloroform, thereby swelling and peptizing the cellulose acetate. This theory was applied by Esselen only to alcohol in chloroform and in benzene as solvents for cellulose acetate, but a similar theory might be applied to nearly all cases in which mixtures of liquids are better solvents than either of the pure liquids.

In an excellent discussion of solvents for cellulose esters, Mardles[5] emphasizes the idea that liquids which are solvents are sufficiently at-

[1] Communication No. 316 from the Research Laboratory of the Eastman Kodak Company.
[2] Guy Barr, and L. L. Bircumshaw, *Trans. Faraday. Soc.*, 16, 99 (1921).
[3] M. L. Byron. *J. Phys. Chem.*, 30, 1116 (1926).
[4] G. J. Esselen, Jr., *Ind. Eng. Chem.*, 12, 801 (1920).
[5] E. W. J. Mardles, *J. Soc. Chem. Ind.*, 42, T 129 (1923).

tracted toward the cellulose ester to form complexes with it. He states that since there is a rapid decrease in solvent power with ascent in a homologous series, there is a decrease in solvent power as the molecular weight increases. Therefore, any addition to the solvent which tends to decrease its association or to simplify the molecular state, increases its solvent power. This brings us back very closely to the theories of

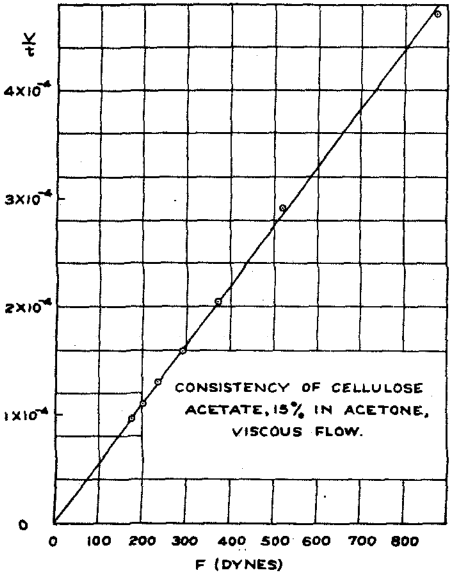


FIG. 1.

Barr and Bircumshaw and of Byron. One objection to Mardles statements might be made. Although it appears to be true that for cellulose nitrate any increase in the molecular weight of a homologous series decreases the solvent power, it is not true for some of the cellulose esters of the higher fatty acids. This will be discussed later. McBain[6] tends to agree with Mardles in so far as both emphasize the solvation as the important factor, but suggests that in a mixture of solvents there

[6] J. W. McBain, *J. Phys. Chem.*, 30, 239 (1926).

are more kinds of molecules to be attracted to different portions of the cellulose molecule, and therefore to solvate it more completely, than there are in a pure liquid.

McBain's general thesis is that any solvent combination which tends to separate the cellulose ester from large ramifying aggregates into small particles which have no attraction for each other is a good

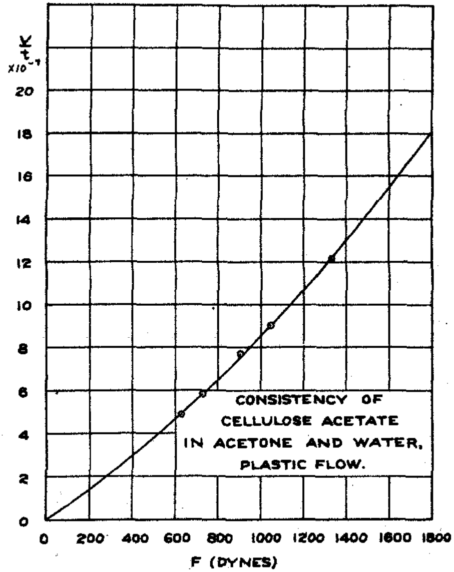


FIG. 2.

solvent, and produces a sol with very little "elasticity" or plasticity; and any liquid which tends to separate them into larger particles or into smaller particles which still have some attraction for each other, is not a good solvent. The idea that large ramifying aggregates are necessary for plasticity has been severely criticized by Hatschek,[7] but nevertheless some such action of the solvent might be illustrated by some measure-

[7] E. Hatschek, *J. Phys. Chem.*, 31, 383 (1927).

ments of the effect of known solvents upon the plasticity of cellulose acetate.

In Figure 1 we have a curve for a cellulose acetate in acetone. It will be observed that the liquid is almost purely viscous, that is, the curvature of the velocity pressure curve is very slight. In Figure 2 we have a curve for a more dilute solution of the same cellulose ace-

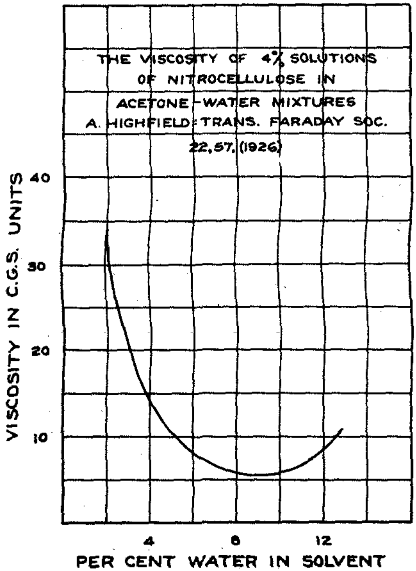


Fig. 3.

tate in acetone and water. It will be noted that the apparent viscosity is practically the same for this solution as for the other, but that the plasticity is considerably greater. This tends to illustrate the idea stated by McBain. If a non-solvent such as water is gradually added to this sort of solution, it can be made to set to a stiff jelly showing still greater plasticity. This idea appears to us to be extremely important in studying the consistency of cellulose esters. In the very best solvents

the particles appear to be so thoroughly dispersed that very little plasticity is shown.

In a very interesting paper containing a large number of viscosity data Highfield [8] has adapted the polar-non-polar theory of Hildebrand [9] to explain the minimum in the viscosity curve of cellulose nitrate in

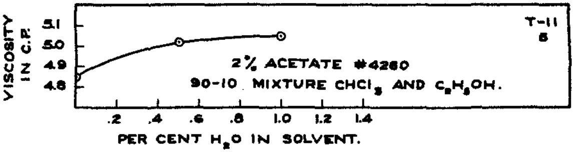


FIG. 4.

acetone-water mixtures. He assumes, with very good evidence, that one particular mixture of acetone and water has the optimum polar characteristics for dissolving nitro-cellulose. No matter what the composition of the acetone-water mixture, the nitro-cellulose aggregates will tend to absorb a mixture containing this optimum ratio. Therefore,

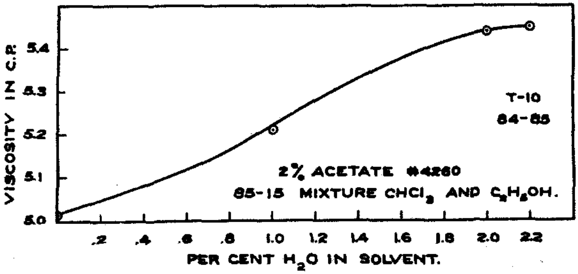


FIG. 5.

for example, if the acetone-alcohol mixture contains less water than the optimum, the nitrocellulose aggregates will be surrounded by a liquid mixture, differing in composition from that of the bulk of the solvent, and this will tend to restrict the free flow of the molecules of the liquid. "With excessive water, the absorbed solvent will be richer in acetone

[8] A. Highfield, *Trans. Faraday Soc.*, 22, 57 (1926).
[9] J. H. Hildebrand, "Solubility," American Chemical Society, Monograph Series. The Chemical Catalog Company, Inc., 1924.

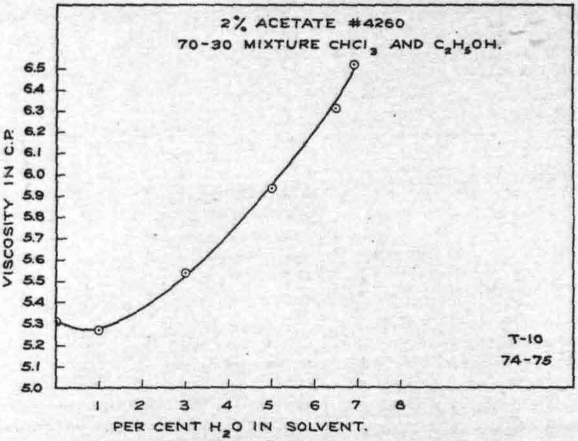

2% ACETATE #4260
70-30 MIXTURE $CHCl_3$ AND C_2H_5OH.
VISCOSITY IN C.P.
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
5.4
5.3
5.2
5.1
5.0
T-10
74-75
1 2 3 4 5 6 7 8
PER CENT H_2O IN SOLVENT.

Fig. 6.

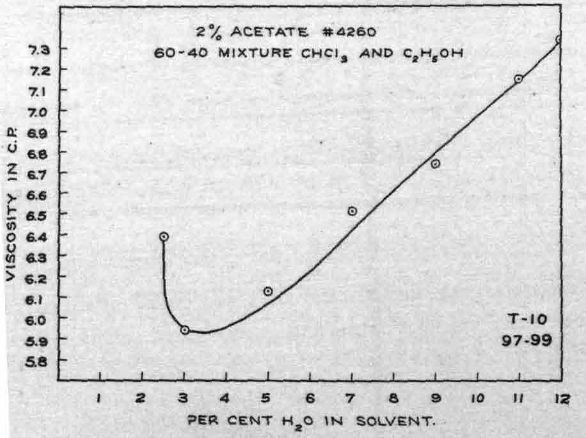

2% ACETATE #4260
60-40 MIXTURE $CHCl_3$ AND C_2H_5OH
VISCOSITY IN C.P.
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
6.1
6.0
5.9
5.8
T-10
97-99
1 2 3 4 5 6 7 8 9 10 11 12
PER CENT H_2O IN SOLVENT.

Fig. 7.

than the remaining solvent. Since these solvent mixtures contain a large proportion of acetone, the difference between the absorbed solvent and unabsorbed solvent will not be so great as in the previous case. The right hand limb of the "U" curve (Fig. 3) is therefore less steep than the left hand limb. With very great excess of water the interfacial tensions between absorbed and unabsorbed solvent results in a separation of the system into two phases with a separating meniscus."

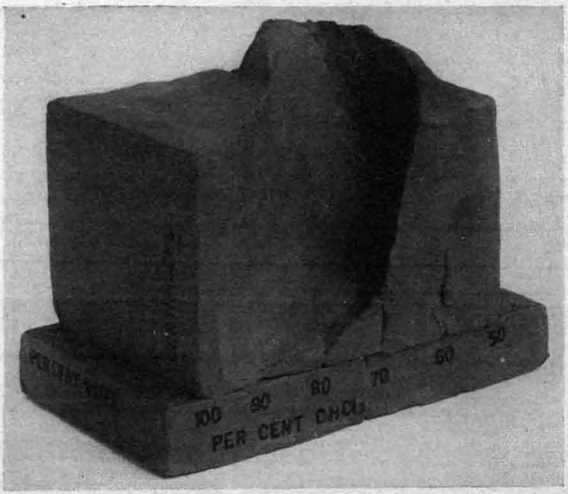


FIG. 8.

Whatever may be said against Highfield's explanation of the mechanism of these viscosity changes, it is difficulty to find any serious objections to the theory in general, namely that there is for every cellulose ester some particular degree of polarity which the solvent must have in order to peptize it thoroughly. It is extremely unlikely that any pure liquid would have exactly the proper degree of polarity to make an optimum solvent for any particular cellulose ester. With two liquids however, one of which has a polarity too great and the other of which has a polarity too small to form an optimum mixture, there will always be a minimum in their viscosity composition diagram.

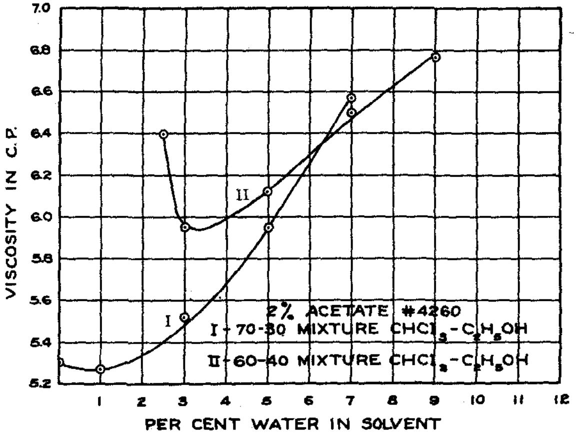

VISCOSITY IN C.P.
PER CENT WATER IN SOLVENT
2% ACETATE #4260
I - 70-30 MIXTURE $CHCl_3-C_2H_5OH$
II - 60-40 MIXTURE $CHCl_3-C_2H_5OH$

Fig. 9.

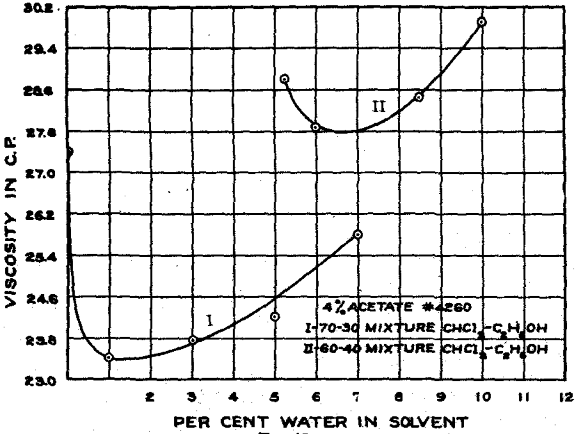

VISCOSITY IN C.P.
PER CENT WATER IN SOLVENT
4% ACETATE #4260
I-70-30 MIXTURE $CHCl_3-C_2H_5OH$
II-60-40 MIXTURE $CHCl_3-C_2H_5OH$

Fig. 10.

With a mixture of two liquids both of which are on the same side of the particular polarity required by the cellulose ester, there would never be such a minimum unless some other effect comes into play. Whether or not the above rule always holds, we cannot at present be sure.

During an investigation of the apparent viscosity of cellulose acetate, an apparent contradiction to this polar-non-polar theory was observed. The apparent viscosities of 2 per cent cellulose acetate in various mix-

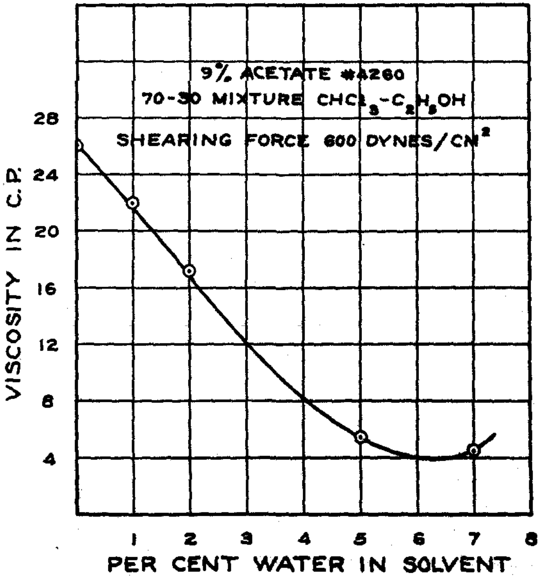


FIG. 11.

tures of alcohol, chloroform, and water were measured. These are shown in Figures 4 to 7 and a space model of the viscosity is shown in Figure 8. It will be observed that the viscosity of a 70-30 chloroform-alcohol mixture is greater than one of an 85-15 mixture. This should mean that the 70-30 mixture is somewhat too polar to be the optimum solvent. Nevertheless, when water is added to this mixture

it is found that the viscosity decreases. The anomaly is this—that when a very polar solvent is added to a solvent which is already too polar, the solvent properties become better. If we assume, however, with Lewis[10] that the "polar characteristic of a substance depends not only upon the specific properties of the individual molecules but also upon what we may call the strength of the polar environment," the theory becomes somewhat more flexible. We can assume that the water, either because it is adsorbed by the cellulose acetate or for other reasons, increases the polarity of the cellulose acetate and therefore makes it soluble in a solvent which was more polar than the optimum polarity for pure cellulose acetate. If the adsorption theory is correct we should expect to find that more water must be added to a 70-30 chloroform-alcohol mixture, to obtain the minimum in the viscosity curve if a concentrated cellulose acetate solution is used, than if a dilute solution is used. That this is so may be seen from Figures 9, 10 and 11.

Whether or not this polar, non-polar theory is the complete story must be left to the future, but certainly most of us use it either consciously or unconsciously at present. No one would hesitate to predict that cellulose stearate would be more soluble in typical non-polar solvents such as benzol or carbon-tetrachloride than would cellulose butyrate or cellulose acetate. No one would hesitate to predict that cellulose triacetate would be more soluble in chloroform than cellulose di-acetate or that cellulose di-acetate would be more readily peptized by acetone than by chloroform. Perhaps the reason that these facts could be so easily predicted is because they are already known, but nevertheless they are in thorough agreement with the polar-non-polar idea of solubility.

Summary

The nature of solvents for cellulose esters has been discussed in relation to their influence on plasticity, without, however, touching on the relationship between mechanical structure and plasticity.

Eastman Kodak Company,
Rochester, N. Y.,

[10] G. N. Lewis, *J. Am. Chem. Soc.*, 38, 762 (1916).

A NEW RAPID EXTRUSIVE TYPE OF PLASTOMETER

By P. M. Giesy and S. Arzoomanian

While the penetrativity of plastometer first proposed by Bingham and Murray[1] and later modified[2] so as to use a mercury column as source of pressure gives a rapid method of measuring plasticity, and has the special advantage of showing unmistakably when slippage through the capillary takes place, it has certain disadvantages. With it one measures directly the linear velocity of the flow of the plastic through the capillary. When this velocity rises above a value of about 2 cm. in 30 sec. the measurement, even with a stop-watch, becomes too inaccurate to be of value. Some plastics, however, at velocities no higher than this give only curved lines; higher velocities must be used if one is to obtain values falling upon the straight portion of the plasticity curve.

To obtain these higher velocities we used at first the reservoir and capillary arrangement of Figure 1 with a mercury column to furnish pressure, weighing the plastic extruded in a measured time. This method was quite time-consuming on account of the many weighings required, and on account of the necessity of making a specific gravity determination if absolute values were desired, but it gave quite satisfactory results.

By combining the principle of the burette consistometer[3] with this apparatus we obtained the present form, shown in Figure 1. In this the mercury column, contained in a burette, serves both as a source of pressure and as a means of measuring the amount of plastic which has flowed through the capillary. The apparatus consists only of standard pipe fittings and ordinary laboratory apparatus. Different sized capillaries may be used, depending on the plastic, and these may be calibrated by any of the usual methods, including that of using them with a standard liquid in a constant-head viscometer.[4] The apparatus is quite rugged in construction. No weighings are required, and the only specific gravity determination required is the rough one (to the second decimal) needed to apply the pressure correction equation (1) given later.

[1] *Proc. Am. Soc. Testing Materials*, 23, II, 655 (1923).

[2] E. Moness and P. M. Giesy, *J. Phys. Chem.*, 29, 1282 (1925); *J. Amer. Pharm. Assn.*, 15, 94 (1926).

[3] Herschel and Bulkley; Ind. & Eng. Chem., 19, 134 (1927).

[4] E. Moness and P. M. Geisy, *J. Phys. Chem.*, 29, 1283 (1925); *J. Am. Pharm. Assn.*, 15, 39 (1926).

The metal parts of the plastometer must be of black iron, as galvanized fittings contaminate the mercury. For the flexible connection between the burette and the reservoir canvas-lined pressure tubing is used, wired fast at the ends. A test showed that the volume of this did not change measurably within the limits of pressure used by us (70 cm. mercury maximum). For the other joints—there should be as few as possible—heavy rubber tubing is used. The parts are butted

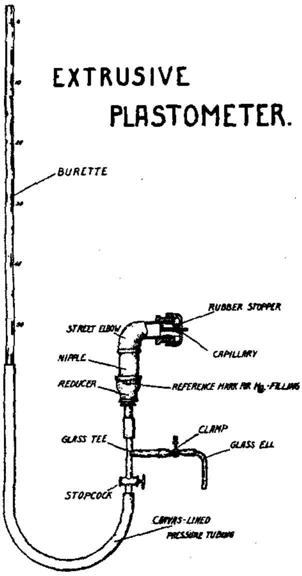


Fig. 1.

closely, the tubing is wired fast, and the joint is then wrapped tightly with friction tape. A one-inch nipple, two and one-half inches long, forms the body of the reservoir; this has a capacity of 35 cc., permitting a pressure drop of about 35 cm. during a run. An ordinary rubber stopper carries the capillary, being held in position by a pipe cap drilled with a hole through which the capillary passes.

In using the plastometer, the street ell is first removed from the

TABLE 1.—TYPICAL DATA SHEET.

Expt. M(1). R = 0.1151 cm. L = 3.90 cm.

Burette Reading V Cc.	Time T Min. Sec.	ΔT Secs.	V_t Cc.	Applied Pressure Cms. Hg.	Pressure Correction Pc Cms. Hg.	Corrected Average Pressure P Cms. Hg.	$\frac{PR}{2L}$ (195.8 P) F Dynes/Sq. Cm.	$\frac{4}{\pi R^3} \cdot \frac{\Delta V}{\Delta T}$ $\left(\frac{1670}{\Delta T}\right)$
0	....	..	..	67.80	...			
1	0:00							
3	0:20	20	2	65.84	1.25	64.59	12,640	88.50
5	0:43	23	4	63.90	1.59	62.31	12,200	72.60
7	1:10	27	6	61.98	1.93	60.05	11,760	61.80
9	1:40	30	8	60.00	2.27	57.73	11,300	55.67
11	2:15	35	10	58.10	2.61	55.49	10,870	47.70
13	2:57	42	12	56.10	2.95	53.15	10,410	39.75
15	3:44	47	14	54.10	3.29	50.81	9,955	35.53
17	4:43	59	16	52.12	3.63	48.49	9,490	28.30
19	5:55	72	18	50.17	3.97	46.20	9,045	23.20
21	7:27	92	20	48.20	4.31	43.89	8,590	18.15
23	9:31	124	22	46.24	4.65	41.59	8,140	13.46
25	12:32	181	24	44.27	5.00	39.27	7,685	9.23
27	17:21	289	26	42.30	5.34	36.96	7,230	5.78
29	33:20	959	28	40.30	5.69	34.61	6,780	1.74

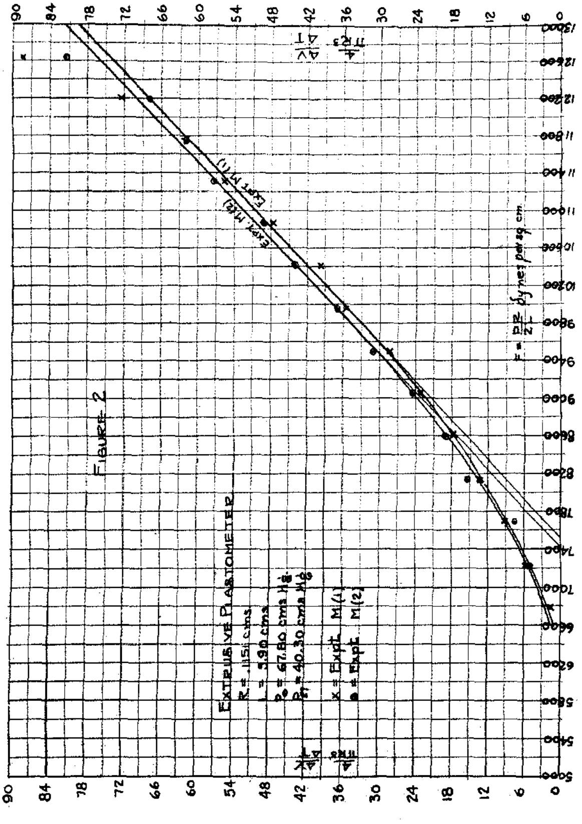


FIGURE 2

nipple and the stopcock between the burette and the reservoir is opened. Mercury is now poured into the reservoir to the reference mark. This is measured by using a cork float with a vertical glass rod attached to its center and on which is filed a scratch mark whose distance from the bottom of the cork stopper is equal to the length from the reservoir reference mark to the upper rim of the plastometer nipple. The stopcock between the reservoir and the burette is now closed, the latter filled with mercury to the zero mark, and the height of the column measured (burette zero to reservoir reference mark). The nipple and street-ell are filled with plastic, taking care to avoid air-bubbles. This is best done by squeezing the plastic from a collapsible tube through a glass tube attached with rubber tubing to the nozzle of the collapsible tube, keeping the end of the glass tube beneath the surface of the plastic already squeezed out. The street ell is then screwed onto the nipple, and the rubber stopper holding the capillary is threaded into place tightly. The stopcock is then opened, the stop-watch started and time readings are taken as the mercury passes the 1, 3, 5, 7, etc., cc. marks. The "applied pressures" are measured as follows:—preliminary to connecting the burette to the apparatus a table is made consisting of the linear distances (in cms.) of each cubic centimeter graduation on the burette from the zero reading. For the calculations we read from this table the linear distance of the mid-point of each interval from the burette zero reading and subtract this value from the linear distance between the zero and the reference mark on the reservoir (i.e., from the initial applied pressure).

At the start of the run the effective pressure at the capillary is the pressure of the mercury column minus the hydrostatic head of the plastic in the plastometer. As the run proceeds, the mercury level falls in the burette and rises in the plastometer, and the hydrostatic head of the plastic diminishes. The following equation gives the correction to be subtracted from the height of the mercury above the reference mark on the reservoir:

$$P_c = V_t \left(\frac{\rho_{Hg} - \rho_p}{\rho_{Hg}}\right)\left(\frac{4}{\pi D^2}\right) + a\left(\frac{\rho_p}{\rho_{Hg}}\right) \qquad (1)$$

P_c = Correction to be subtracted (cms. Hg.)
V_t = Burette reading at mid-point of interval
ρ_{Hg} = Specific gravity of mercury
ρ_p = Specific gravity of plastic
D = Inside diameter of plastometer nipple (cms.)
a = Height of axis of capillary above reference mark on reservoir (cms.)

For a definite plastometer and a definite plastic, this reduces to the form

$$P_c = m V_t + n \quad \text{(where } m \text{ and } n \text{ are constants)} \qquad (2)$$

which is the equation of a straight line, and can be plotted once for all.

In plotting our results, we plot $\frac{4}{\pi R^3} \cdot \frac{\Delta V}{\Delta T}$ as a function of $F = \frac{PR}{2L}$, R and L being measured in cms., ΔV in cc., ΔT in sec., and P in dynes per sq. cm. The slope of the asymptote to the curve then gives us directly the mobility in rhés; the x-intercept, which is in dynes per sq. cm., is a measure of the yield value. We have probably not carried our velocities high enough to get the true asymptote to the curve, but for control work this is not necessary. Provided the same pressure range is always used, the results obtained will show any variation in consistency from the normal.

Table 1 gives the data of a typical run. The first, fourth, fifth, sixth, seventh, and eighth columns are the same for all runs, as long as the set-up of the apparatus and the density of the plastic (to two decimals) remain constant. The second column holds the readings made in the run, and the third and last must be calculated for each run. For a given capillary the values of the last column equal const./ΔT. Thus very little calculation is required when the method is used for control work. In this particular case, P_c is read from the graph of equation (2). Sample:

$$F = \frac{PR}{2L} = \frac{P \times 13.54 \times 980 \times 0.1151}{2 \times 3.90} = 195.8\,P \text{ dynes per sq. cm.} \quad (3)$$

$$\frac{4}{\pi R^3} \cdot \frac{\Delta V}{\Delta T} = \frac{4}{\pi (0.1151)^3} \cdot \frac{2}{\Delta T} = \frac{1670}{\Delta T}. \quad (4)$$

Figure 2 shows the plot of the results of Expt. M(1) (crosses), and a check run on the same material, M(2) (circles). We do not believe that the slight variation between these two runs was primarily due to defects in our method. The plastic we were working with contained a small amount of sodium stearate, and therefore possessed some structure. It was impossible to fill the plastometer without breaking this down to a greater or less extent. The effect of this was shown by some check runs made without refilling the street ell with fresh, undeformed plastic. These runs gave values of the mobility approximately 50 per cent higher than runs made when the whole plastometer was filled with fresh plastic.

We used no bath to control temperature, making all runs at room temperature, but see no reason why a constant temperature bath cannot be used.

Research Laboratories,
E. R. Squibb & Sons,
Brooklyn, N. Y.

THE FALLING SPHERE VISCOMETER AND PLASTICITY MEASUREMENTS[1]

By H. E. Phipps

The falling sphere viscometer has been used rather extensively in measuring the viscosity of rather viscous liquids.[2, 3] It can be used to obtain either absolute or relative viscosity and is both rapid and simple in operation.

A number of these rather thick liquids, such as solutions of cellulose acetate or nitrate, cellulose in Schweitzer's reagent, and others of this general type, are not simply viscous, but plastic. That is, the rate of flow of one liquid layer over another is not strictly proportional to the shearing force applied. This means that many measurements made on solutions of the above mentioned type with the falling sphere viscometer would have been different in value if another kind of sphere had been used. From this it appeared that it should be possible to obtain a plasticity curve with the falling sphere viscometer by using spheres of the same volume but different densities, or different volumes and the same or different densities. It was thought that the former method would be dimensionally simpler.

If the rate of fall of the sphere is plotted against $d - \rho$, where d is the density of the sphere and ρ that of the liquid, the curve obtained should show what type of liquid is being observed. If the result is a straight line passing through the origin, no plasticity will be shown. If the straight line intersects the x axis at a point to the right of the origin, simple plasticity will be shown, with a definite yield value and mobility. If the line passes through the origin but curves steadily upward, the sort of plasticity which is commonly observed in solutions of cellulose esters would be indicated.

Experimental

The apparatus consisted of a glass tube some 100 cm. long and 3.0 cm. in inside diameter, standing in a water jacket regulated to 25° C. $\pm$ 0.1°. The tube was graduated every 5 cm. The time was taken by means of a stop-watch, reading to 0.1 seconds, which had been checked against an accurate clock. The spheres used, with the exception of glass

[1] Communication No. 317 from the Research Laboratory of the Eastman Kodak Co.
[2] S. E. Sheppard, *J. Ind. Eng. Chem.*, 9, 528 (1917).
[3] W. H. Gibson and L. M. Jacobs, *J. Chem. Soc.*, 117, 473 (1920).

and steel, were made by the tool room of the Eastman Kodak Company, Rochester, N. Y. They were turned out on a lathe, using wooden chucks for the softer materials and a special, automatic feed, cutting tool. The diameters were 0.3175 cm. or ⅛″ and were accurate to within 0.6 *per cent.* The spheres were of the following kinds:

	Mass	Density
Amber	0.0185 ± 0.0001 gms.	1.068
Bakelite	0.0229 ± 0.0001 "	1.357
Ivory	0.0333 ± 0.0001 "	1.987
Glass	0.0424 ± 0.0002 "	2.515
Tin	0.1256 ± 0.0002 "	7.42
Steel	0.1307 ± 0.0002 "	7.73
Copper	0.1512 ± 0.0002 "	8.93
Silver	0.1786 ± 0.0004 "	10.61
Tantalum	0.2806 ± 0.0004 "	16.60

Typical results are shown in Figure 1 with castor oil, and Figure 2 with cellulose acetate solutions. The viscosity of castor oil was calculated for each class of sphere by means of Ladenburg's equation [3] to further check the spheres. The equation follows:

$$\eta = \frac{2}{9} \frac{gr^2(d-\rho)T}{s\left(1+2.4\,\frac{r}{R}\right)\left(1+3.3\,\frac{r}{h}\right)}$$

where r, d, and s are respectively the radius, density and distance of fall of the sphere, ρ and h are the density and height of liquid, R the radius of the tube, T the time, and g the gravitational constant. The term $\frac{r}{R}$ should be 0.1 or less. The viscosity obtained in this manner was 7.10 poises, with a maximum variation of 0.7 per cent. This was regarded as very good considering the high velocities of the heavier spheres. The value obtained with the Ostwald viscometer was 7.20 poises.

Discussion of Results

Figure 1 is certainly the type of curve to be expected when working with a viscous liquid. Figure 2 is of the same general type of curve shown in Figure 3, which was obtained with the Bingham and Murray plastometer,[4] using the same cellulose acetate solution.

In Figure 4, the viscosities of the cellulose acetate solution obtained with the Bingham and Murray were plotted as ordinates and the shearing force as abscissæ. The viscosities obtained with the falling-sphere instrument are similarly plotted, but no definite value was assigned as shearing force, the η's being so placed on the F axis that a continuous

[4] E. C. Bingham and H. A. Murray, Jr., *J. S. T. M.*, 23, II, 655 (1923).

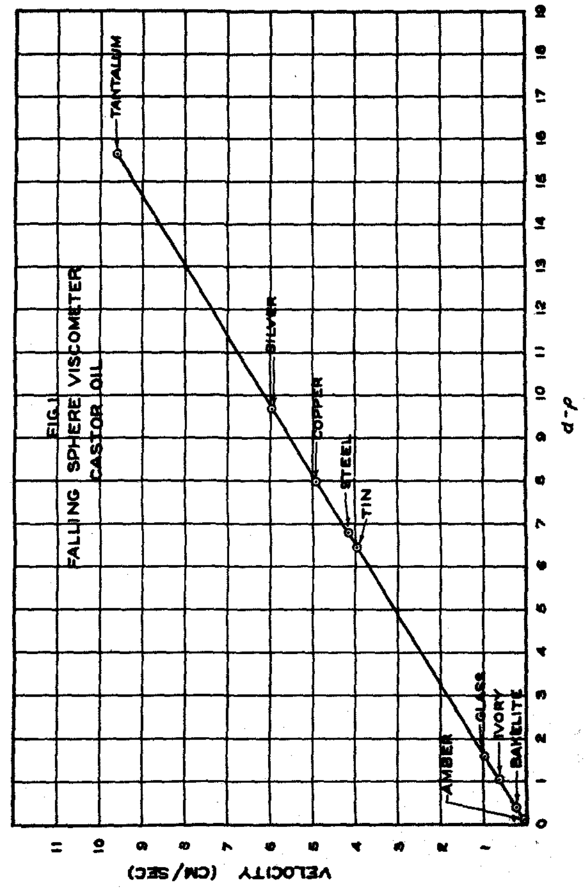


FIG. 1
FALLING SPHERE VISCOMETER
CASTOR OIL
TANTALUM
SILVER
COPPER
STEEL
TIN
AMBER
GLASS
IVORY
BAKELITE
VELOCITY (CM/SEC)
d - ρ
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19

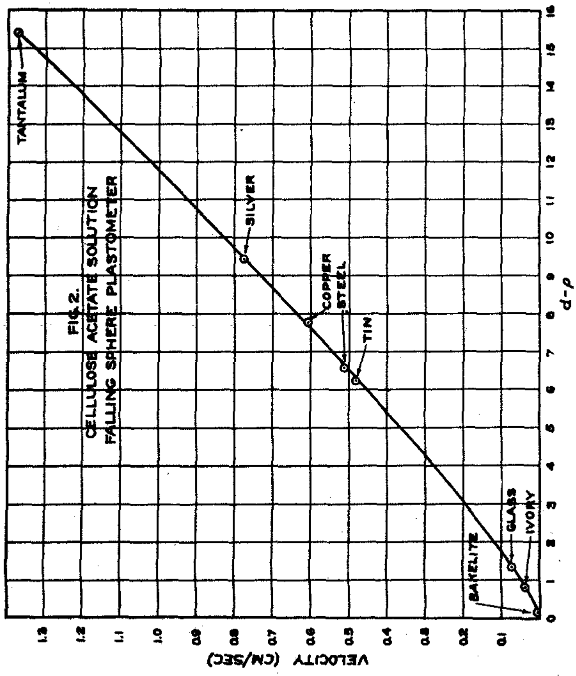


FIG. 2.
CELLULOSE ACETATE SOLUTION
FALLING SPHERE PLASTOMETER

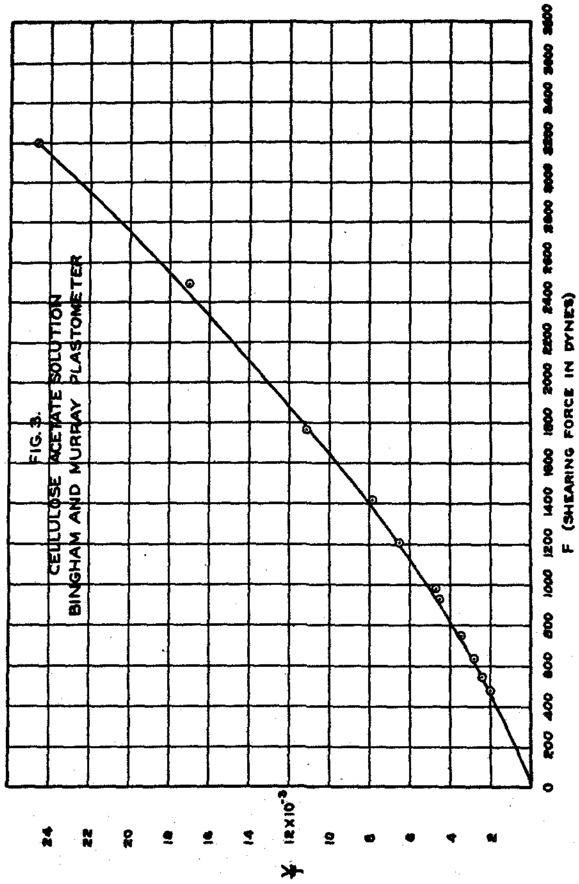


FIG. 3.
CELLULOSE ACETATE SOLUTION
BINGHAM AND MURRAY PLASTOMETER
F (SHEARING FORCE IN DYNES)
0 200 400 600 800 1000 1200 1400 1600 1800 2000 2200 2400 2600 2800 3000 3200 3400 3600 3800
2 4 6 8 10 12X10^{-3} 14 16 18 20 22 24
ψ

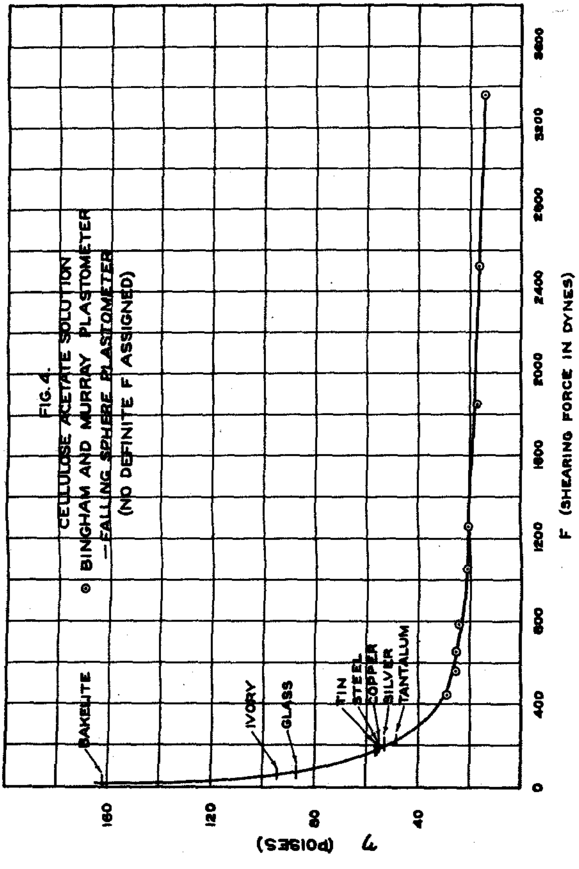


FIG. 4.
CELLULOSE ACETATE SOLUTION
⊙ BINGHAM AND MURRAY PLASTOMETER
— FALLING SPHERE PLASTOMETER
(NO DEFINITE F ASSIGNED)
BAKELITE
IVORY
GLASS
TIN
STEEL
COPPER
SILVER
TANTALUM
160
120
80
40
η (POISES)
0
400
800
1200
1600
2000
2400
2800
3200
3600
F (SHEARING FORCE IN DYNES)

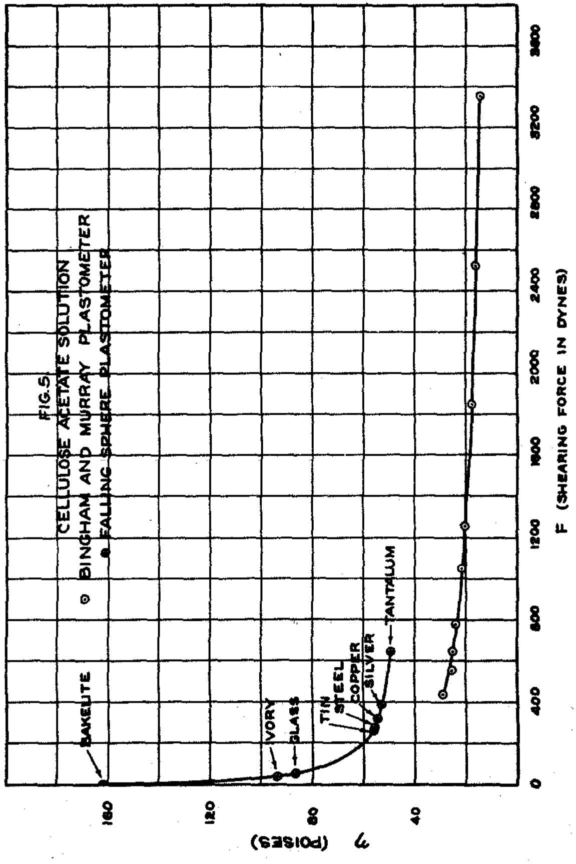


FIG.5
CELLULOSE ACETATE SOLUTION
⊙ BINGHAM AND MURRAY PLASTOMETER
● FALLING SPHERE PLASTOMETER
BAKELITE
IVORY
GLASS
TIN
STEEL
COPPER
SILVER
TANTALUM
160
120
80
40
η (POISES)
0
400
800
1200
1600
2000
2400
2800
3200
3600
F (SHEARING FORCE IN DYNES)

curve is obtained. This indicates that the shearing force applied by the spheres is very low when co-related to the F used in the capillary tube method. However, if we calculate the maximum force exerted between any two layers of the liquid, or rather, the tangential force exerted on the walls of the spheres in a manner analogous to that used by Bingham in calculating his F for capillary tubes ($F = \frac{Pr}{2L}$, where P is the pressure in dynes, r the radius, and L the length of the capillary), we would use the Stokes' law equation[5] in the form $F = \frac{3}{2}\frac{\eta V}{r}$, where V is the velocity. This gives a curve (Fig. 5) which does not coincide with the one obtained with the Bingham and Murray plastometer. The reason for this discrepancy appears to be that in the falling sphere viscometer a larger fraction of the energy is dissipated in portions of the liquid where the shearing force is very small than in the case of the capillary tube viscometer. This makes the true viscosity-force curve somewhat more difficult to obtain than with the capillary-tube method, but does not mean that the instrument will be less valuable from a practical standpoint. Its usefulness lies in its ability to give information about the extreme lower portion of an ordinary plasticity curve, a portion which is very hard to investigate with other types of plastometers because of experimental difficulties, and also in the rapidity and ease of operation.

Conclusions

1. The falling sphere viscometer can be used as a plastometer.
2. Its use is limited to the lower portion of a normal plasticity curve.

The author wishes to express his appreciation for the valuable suggestions made by Dr. S. E. Sheppard and Dr. E. K. Carver and for the experimental assistance given by Dr. R. C. Houck of this Laboratory.

Eastman Kodak Company,
Rochester, N. Y.

[5] Lamb's "Hydrodynamics," 3rd Edit. Camb. Univ. Press 1906, p. 552.

THE FALLING BALL METHOD FOR THE MEASUREMENT OF APPARENT VISCOSITY OF NITROCELLULOSE SOLUTIONS

BY JOHN K. SPEICHER AND G. H. PFEIFFER

The falling ball method of viscosity determination has enjoyed wide use in industrial laboratories for a number of years, particularly for control of the manufacture and use of nitrocellulose. The method has a number of advantages: it is rapid, the manipulation is extremely simple, apparatus of high accuracy can be secured easily and cheaply, and results can be duplicated closely.

In spite of the wide use of the method very little data have ever been published showing, as applied to nitrocellulose, (1) the effects of slight variations in apparatus and manipulation; (2) the relation between results obtained using widely differing tubes and balls; (3) the relation of falling ball results to results on other types of viscometers. Sheppard[1] has given some interesting results on the application of this method to nitrocellulose solutions.

The data presented here were secured with the object of determining the range, accuracy, and general adaptability of the method rather than that of securing fundamental knowledge of the flow of nitrocellulose solutions. It is quite well established that nitrocellulose solutions do not obey the conventional laws of flow of viscous liquids. For this reason the word viscosity cannot apply. Since the method used gives results in terms of viscosity the results will be called such, it being understood that apparent viscosity, under the conditions specified, is meant.

The falling ball method of determining viscosity is based on Stokes' law for the velocity of a small sphere falling through a liquid of infinite extent. However, the simple law of Stokes does not hold when the extent of the liquid is limited by a cylindrical vessel. Ladenburg[2] has added two linear corrections for wall effect and end effect. The modified equation according to Ladenburg is:

$$N = \frac{2\,Gr^2\,(D - d)\,T}{9S\left(1 + 2.4\frac{r}{R}\right)\left(1 + 3.3\frac{r}{H}\right)}$$

When N — viscosity in poises
r — radius of ball
D — density of ball
d — density of liquid

[1] *J. Ind. Eng. Chem.*, 9, 523 (1917).
[2] *Ann. Phys.*, 23, 9, 447 (1907).

T — time of fall
S — distance for which T is measured
R — radius of cylinder
H — height of liquid

Gibson and Jacobs [8] using castor oil showed by experiment that the above equation does apply provided the radius of the ball is small in comparison to the radius of the cylinder. An experiment similar to that of Gibson and Jacobs gave rather close agreement between tubes of varying diameter but not such good agreement with the known viscosity of the oil.

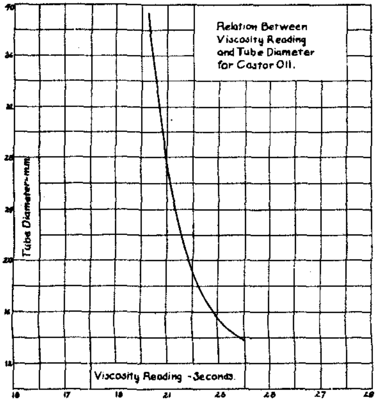


FIG. 1.

All of the work has been done at 25° C. In the case of nitrocellulose it was found that a difference in temperature of 0.1° C. caused a change in viscosity of about 0.5 per cent. More specifically:

$$\log T = \log T_1 + 0.0207\ (t_1 - t)$$

where T and T_1 are readings obtained at temperatures t and t_1.

Correction for Wall Effect.—Using a highly purified sample of castor oil the viscosity of which had been determined by Dr. Bingham to be 665.2 centipoises the results given in Table 1 were obtained. Steel balls 1.587 mm. (1/16 inch) in diameter were used in tubes 38 cm. long, the distance between marks being 25.4 cm. In Figure 1 readings are plotted against the diameter.

[8] *J. Chem. Soc.*, 117, 473-478 (1920).

TABLE 1.—VISCOSITY OF CASTOR OIL BY FALLING BALL METHOD.

Diameter of Tube (Mm.)	Time of Fall (Sec.)	Viscosity (Centipoises)
14.80	23.4	693.
21.61	21.7	677.
24.91	21.5	684.
27.33	21.2	683.
29.76	20.7	673.
31.64	20.6	674.

The same or better agreement between tubes was obtained using nitrocellulose solutions. A considerable number of samples of nitrocellulose were used with the same general result in each case. Table 2 gives a few specimen results for solutions containing by weight, 12.2 per cent nitrocellulose, 22 per cent ethyl alcohol, 17.5 per cent ethyl acetate, 48.3 per cent benzol, except the solution of ½″ R.S. which is 20 per cent nitrocellulose in the same solvent mixture.

TABLE 2.—CALCULATED VISCOSITIES OF NITROCELLULOSE SOLUTIONS IN TUBES OF DIFFERENT DIAMETERS, USING LADENBURG'S CORRECTIONS.

	1/2″ R.S.		15″		20″		80″	
Diameter of Tube Mm.	Time Sec.	Viscosity Centipoises	Time Sec.	Viscosity Centipoises	Time Sec.	Viscosity Centipoises	Time Sec.	Viscosity Centipoises
21.61	16.0	499.2	178.5	5568	281.2	8772	1115	34790
24.91	15.6	496.6	171.7	5467	270.0	8596	1065	33910
27.33	15.3	492.9	169.5	5460	265.7	8559	1043	33600
29.76	15.2	494.6	167.0	5434	264.0	8590	1030	33515
31.64	15.1	494.7	166.7	5460	262.7	8606	1020	33410
43.30	15.0	506.1	162.0	5465	258.0	8684	990	33400

Ratio Between Readings Using Balls of Different Diameters.— It was found that for any one tube the ratio between the reading obtained with a 1/16 inch steel ball and a 5/16 inch steel ball was constant. Within the limits investigated the ratio was found to be independent of the nitrocellulose used or the viscosity of the solution. The ratio is lower for a small tube than for a large tube. Results for two tubes are given in Table 3.

TABLE 3.—RATIO OF READING OF 1/16″ AND 5/16″ BALLS.

Tube Diameter 27.33 Mm.			Tube Diameter 21.60 Mm.		
5/16″ Reading Seconds	1/16″ Reading Seconds	Ratio	5/16″ Reading Seconds	1/16″ Reading Seconds	Ratio
4.80	62.20	12.96	1.60	15.90	9.94
9.10	117.80	12.94	17.60	178.80	10.15
12.60	162.80	12.92	28.20	281.30	9.97
33.85	435.20	12.86	109.20	1088.60	9.95
77.95	1006.80	12.91	230.00	2320.00	10.09

Figure 2 was obtained by plotting such ratios against tube diameter. The significance of these data are that all types of nitrocellulose tested, regardless of viscosity, give the same ratio and that as the tubes become

larger the ratio is rapidly approaching the theoretical value as calculated from Stokes' Law.

Maximum Velocity of Ball.—It is recognized that if the viscosity of a solution is low the velocity of the descending ball will be so great that Stokes' Law will fail to apply. Tests were made using solutions of various viscosities, including some very low ones in tubes over six feet high, the height being necessary to minimize errors in reading the time. It was found that the ratio between readings with different balls remained constant even when the velocity was as high as 30.6 cm. per second. Furthermore it was found that the velocity of the ball was

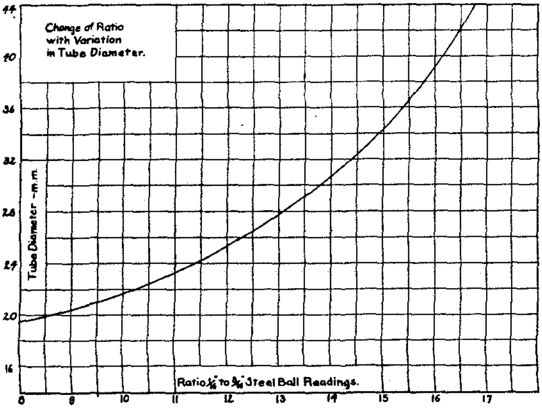


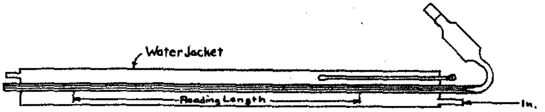
FIG. 2.

constant throughout the length of the tube. It is apparent then that Stokes' Law still applies at velocities which are higher than it is practical to use because of the large influence of inaccuracies in measurement of time over short intervals.

Relation Between Falling Ball and Capillary Tube Results.—In all of the data up to this point nothing was found to indicate any variation in the type of flow between widely different types of nitrocellulose. The difference in the effective force resisting the fall of a $5/16$ inch and a $1/16$ inch ball is 125 to 1. The actual shearing stresses however may be very small in both cases; consequently if rate of flow were plotted against shearing force the points obtained with the two balls would possibly be very close together, in which case the plastic properties

of nitrocellulose would not be apparent. Comparison of results with those obtained in a capillary tube viscometer showed some variations.

In order to facilitate rapid work a simple viscometer was arranged which gave comparative results only. The viscometer might be considered as an adaptation of the Bingham and Murray plastometer. A tube about 50 cm. long is enclosed in a water jacket and mounted on a



CAPILLARY TUBE VISCOMETER.
Fig. 3.

hinged base. A small reservoir is welded to the tube at an angle of 45° as shown in Figure 3. The operation consists of raising the tube until the reservoir is vertical, filling the reservoir to the mark and lowering the tube to an exactly horizontal position. The particular tube used was approximately 2 mm. in diameter and the reading was taken as the time required to fill the capillary between marks 30 cm. apart. Temperature control to ± 0.05° C. was secured by circulating water from a constant temperature bath through the jacket.

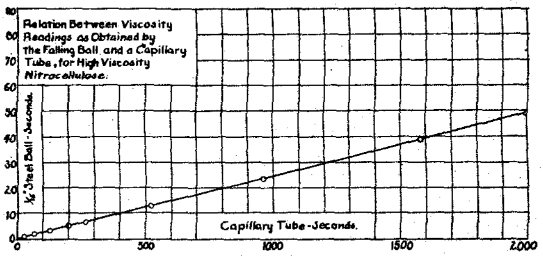


Fig. 4.

tion of the solution, with consequent change of viscosity the ratio for a

The viscometer was calibrated, for purposes of comparison with the falling ball method, by running the same sample of castor oil previously mentioned. Using a 25 mm. tube and a $\frac{1}{16}$ inch steel ball as standard for the falling ball method the ratio between the capillary tube reading and the falling ball reading was 37.30.

Using nitrocellulose solutions the ratio seems to depend on the type of nitrocellulose used. For medium and high viscosity types the ratio

in every case was close to 40.8. For the very low viscosity types, recently developed commercially for use in lacquers, the ratio was 37.35, or practically the same as for castor oil. Regardless of the concentra-

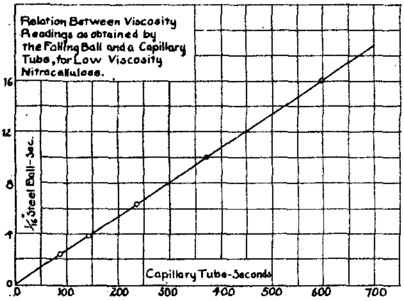


FIG. 5.

given nitrocellulose remains practically constant as indicated by the straight lines shown in Figures 4 and 5.

Starting with the medium viscosity types and going up through the higher viscosity types the ratio apparently remains very nearly constant for samples covering a fairly wide range of viscosity. The extremely high viscosity materials sometimes used in high explosives were not included in the investigation.

SUMMARY

Using the falling ball method, and calculating results by Stokes' Law as modified by Ladenburg, results consistent among themselves were obtained with nitrocellulose solutions.

Very low viscosity types of nitrocellulose produce solutions which not only give consistent results by the falling ball method but also show the same relation between the falling ball method and a capillary tube method that castor oil shows.

With the higher viscosity nitrocelluloses a change in shearing stress as represented by a change from the falling ball to a capillary tube viscometer gives a relation different from castor oil.

The capillary tube instrument used was not a highly enough refined instrument to justify more than comparative measurements; consequently the results cannot be interpreted in terms of absolute values.

Hercules Experimental Station,
Kenvil, N. J.

THE CELLULOSE NITRATES[1]

By James Craik

The existing literature on the subject of the cellulose nitrates is already very extensive and much painstaking work has been done by many investigators in attempting to explain the complex nature of the results obtained in this field. In spite of this fact, there is a surprising lack of unanimity among these earlier workers as to the number and properties of the products formed during the esterification of cellulose by means of mixed nitric and sulfuric acids. This, of course, is not surprising when we consider the difficulties encountered in such a chemical reaction. Although, in the main, the product contains a mixture of cellulose nitrates, there may also be present nitrates of hydrocellulose, oxycellulose and nitrated decomposition products. It must too be borne in mind that the temperature, amount of water present, time of immersion in the nitrating mixture and the proportion of sulfuric to nitric acids play an important part in the final product. Further, no pure homogeneous cellulose nitrate has so far been isolated.

It was in the hope of throwing some light on the properties and number of the cellulose nitrates that the present work was undertaken. Professor Bancroft suggested that an adequate study of their colloid properties ought to do much to advance our knowledge in this work. In addition, some years ago, M. W. Bray, working at Cornell, commenced a research in this field and the preliminary experiments showed that pursuance of this scheme was likely to lead to encouraging results.

Historical

At this point it may be well to give a very brief review of some of the existing theories dealing with the number of cellulose nitrates.

In 1846 Gaudin[2] stated that pyroxylin consisted of two different substances of the same composition, one insoluble in rectified ether, the other soluble, called by him *etherzilin*. He effected a separation in this way, finding that the two components differed in nitrogen content.

[1] The present article is based on investigations undertaken by the author while holding a Commonwealth Fund Fellowship at Cornell University; he wishes to take this opportunity of expressing his indebtedness to the Fund for affording him these facilities.

[2] *Compt. rend.*, 23, 1100 (1846).

Some years later Hadow [3] published elaborate methods for the preparation of three cellulose nitrates to which he ascribed the formulae,

$$C_{12}H_{7},\ 3NO_{4}.O_{10},\ C_{36}H_{22},\ 8NO_{4}.O_{30},\ \text{and}\ C_{36}H_{28},\ 7NO_{4}.O.$$

Martin [4] in 1861 postulated four products, and, eight years later, there appeared the evidence of Gintl [5] that nitrocellulose was to be "considered as a neutral ester of nitric acid with the complex $C_6H_{12}O_6$, the latter being an alcohol with three OH groups." Next followed the results of the investigations made by Wolfram [6] who says, very truly, that "up to the present time a certain amount of doubt exists as to the proper formula of pyroxylin." He reviews the formulae given by Pelouze,[7] Schönbein and Böttger,[8] Péligot [9] and others; [10] then, with a view to elucidating the problem, shows that, by regarding trinitrocellulose, or when doubled the hexanitrocellulose, as the highest stage in nitration, six compounds are possible, the mono-derivative containing 12.49 per cent NO_2 and the hexa- $(C_{12}H_{14}6(NO_2)O_{10})$ containing 46.76 per cent NO_2.

The cellulose nitrates of Eder [11] next deserve mention. This author showed conclusively that "all pyroxylins must be looked upon as nitric esters" and claimed that the lower nitrates could be produced from the higher derivatives, by treatment with dilute nitric acid, alkali, or ammonia. He failed to obtain a mononitrate but gave methods for the preparation of five products, from the di- (6.75% N) to the hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$, (14.14% N). These, with the exception of the last, were soluble in a mixture of ether and alcohol. Vieille [12] took exception to the hexanitrate of Eder on the grounds that a product containing 14.14 per cent nitrogen was never obtained in actual practice; to explain this and his own results he doubled the above formulae, postulating eight cellulose nitrates, the highest of which (13.48% N) he designated the endecanitrocellulose (C_{24} . . .). As is now known, *it has been shown by later workers* [13] *that* 13.48 *per cent does not represent the highest obtainable nitrogen content.*

In 1901 Lunge,[14] in collaboration with Bebie and Weintraub, published the results of very careful work undertaken in the hope of elucidating the problem of obtaining a nitrate with definite nitrogen content

3 *J. Chem. Soc.*, 7, 200 (1854).
4 *Rép. Chimie appliquée*, 3, 257 (1861).
5 *J. prakt. Chem.*, 107, 478 (1869).
6 *Dinglers Polyteck. J.*, 230, 45 (1878); *J. Chem. Soc.*, 36, 218 (1879).
7 *Compt. rend.*, 24, 2 (1847); 23, 892 (1846).
8 *Pogg. Ann.*, 70, 320 (1847).
9 *Compt. rend.*, 23, 1085 (1846).
10 Schmidt and Hecker, *J. prakt. Chem.*, 40, 204 (1847); van Kerckhoff and Reuter, *ibid.*, 40, 262 (1847); Porret and Teschemacher, *Phil. Mag.*, 30, 278 (1847); Domonte and Menard, *Compt. rend.*, 23, 1087 (1846); 24, 390 (1847); Hadow, *loc. cit.*
11 *Ber.*, 13, 169 (1880).
12 *Compt. rend.*, 95, 132 (1882).
13 Hoitsema, *Z. angew. Chem.*, 11, 173 (1898).
14 *J. Am. Chem. Soc.*, 23, 528 (1901).

and properties, by varying the constituents of the nitrating bath. These painstaking researches, without doubt, form one of the most valuable contributions to the methods for the preparation of the nitrates of cellulose. Saposchnikoff [15] claimed that the non-homogeneity of nitrocelluloses was due to the dilution of the nitrating mixture by the water formed in the reaction, the external parts of the mass being more highly nitrated than the inner parts. The final degree of nitration, he asserted, was influenced by the reversibility of the process. In the same year Hake and Bell [16] said that each acid endeavored to carry out its characteristic function, "the sulphuric acid to dissolve and the nitric acid to form esters," to which Crane and Joyce [17] added "that the water endeavors to carry out its characteristic function of hydration and hydrolysis, depending upon the amount present in the mixed acid." Piest [18] was of opinion that the properties of the final product depended largely on the treatment of the original cellulose.

In more recent years De Bruyn [19] inferred from his experimental work on stability and solubility that there exist simple cellulose nitrates with 12.0 and 12.5 per cent nitrogen respectively. In addition, he expressed agreement with the investigations of Vieille (invalidating some of Eder's work), and showed that the substance containing 12.75 per cent nitrogen is present as a mixture of the two isomerides one of which is soluble, the other insoluble in an ether-alcohol mixture. Kugelmass [20] studied the physical properties of solutions of cellulose nitrate (11.9% N), prepared at low temperatures in ether and in alcohol. The estimation of the nitrogen content of the solute, in each case, showed 11.2 and 14.02 per cent respectively, his conclusions being that the dinitrate is dissolved by ether and the alcoholic solution contains the cellulose trinitrate.

Although the foregoing historical review can in no way pretend to be exhaustive it will readily be granted that this portion of the subject is in such a state of chaos as to render any accurate conclusions or generalisations impossible. Great credit, of course, is due to these early and indefatigable investigators, but, it seems that their conclusions, in many cases, were based on very slender grounds. Realising the complex molecule of cellulose with its free hydroxyl groups, and knowing that the nitration of cellulose is a progressive phenomenon, it may seem logical to infer that there are as many as twelve or even more simple cellulose nitrates. The main reasons of previous workers for this assumption, however, have depended on the large number of prod-

[15] *J. Russ. Phys. Chem. Soc.*, 41, 1712 (1909); *J. Chem. Soc.*, 98, 156 (1910).
[16] *J. Soc. Chem. Ind.*, 28, 457 (1909).
[17] *J. Soc. Chem. Ind.*, 29, 540 (1910).
[18] *Z. angew. Chem.*, 23, 1009 (1910).
[19] *Rec. trav. chim.*, 40, 682 (1921).
[20] *Rec. trav. chim.*, 41, 751, 755 (1922).

ucts isolated with varying solubilities in orgånic solvents. Based on the experimental evidence now submitted, it is the opinion of the author that this can be explained more satisfactorily on physical rather than chemical grounds. At any rate, in the light of our present day knowledge of colloid chemistry, and with the advancement of the constitutional studies of the polysaccharides it seems that an attempt to interpret the results from this standpoint is at least justifiable.

Outline of Method

In the course of the present work several specimens of cellulose nitrates have been carefully prepared; those most frequently employed have been (*a*) 8-9 per cent nitrogen, insoluble in ether-alcohol,[21] (*b*) 11.5-12.5, per cent nitrogen, completely soluble in ether-alcohol, and (*c*) 13.0-13.5 per cent nitrogen, insoluble in above solvent mix. Using acid mixes of various concentrations and proportions, attempts have been made to denitrate or "nitrate up" these compounds on the surface. The solubilities in ether-alcohol and acetone, as well as the nitrogen content of the original products were very carefully ascertained. After subjecting to the denitrating or nitrating process, thorough washing and drying, the new samples were against investigated for nitrogen content and solubilities in the above solvents. In this way it has been possible to draw certain conclusions from these data which are now submitted.

Experimental Part

The material used throughout this research was "pure grade surgical absorbent cotton." Before use the cotton was treated with a 3 per cent solution of sodium carbonate at the boiling point for 30 minutes. On filtering and thorough washing, it was extracted with boiling alcohol (95%) and finally with ether. It was dried in an oven at 100° C. for one hour and stored in a desiccator over sulfuric acid until used. An analysis of the purified cotton per 100 grams showed:

Ash, mineral matter, etc.	0.029
Wax, oils, etc.	0.046
Moisture	1.34
Copper value[22]	0.32

Method of nitration.—The nitrations were carried out in a modified form of nitrating vessel, described by Lunge.[23] After placing the

[21] Throughout this paper the term ether-alcohol, when referring to the work of the author, stands for 2 parts ether, 1 part alcohol by volume. The standard of solvents used is described in the experimental part.
[22] According to Schwalbe; indicates percentage of metallic copper.
[23] *Loc. cit.*

cotton (usually 15 or 20 grams) in the vessel it was evacuated to approximately 20 mm. The acid, previously heated or cooled to the required temperature, was slowly added and the whole stored at the nitrating temperature for the specified time.

Washing and drying of cellulose nitrates.—These are the two most important points in the preparation of good samples of nitrated cotton. Unless time is taken with these it is almost useless to carry out any work—a fact which has probably caused much of the conflicting evidence in this field. It was necessary to wash, with frequent changes, in distilled cold water for two days, and for one day in hot water. After removing the excess water, by pressing between sheets of filter paper, the product was partially dried for one hour in an oven at 35-40° C., and finally in a desiccator over sulfuric acid for 7-8 days. The drying oven described by Lunge gave good results but the above method was always adopted where time permitted.

Estimation of nitrogen content.—The analyses of the esters were carried out in a modified form of the Du Pont and Lunge nitrometers, but the method was the standard one employed. The weight of sample analyzed was 0.40-0.43 gram.

Determination of solubility in ether-alcohol and acetone.—Anhydrous ether, absolute alcohol, and acetone, free from methanol—all previously redistilled—were used for this purpose. The procedure in ether-alcohol solubility was: 0.5 gram of the cellulose nitrate was treated in a stoppered flask with 33 cc. of alcohol and allowed to stand for 30 minutes; 67 cc. of ether were then added and the whole shaken at frequent intervals for two hours. The insoluble residue, after being washed well with ether-alcohol, was collected in a Gooch crucible, dried at 100° C. and weighed.[24] The method with acetone was similar, the sample being shaken at intervals for two-and-a-half hours.

Acid mixes.—The different acid mixes were made up from weighed quantities of nitric acid of specific gravity 1.483, sulfuric acid of specific gravity 1.835, and water.

Acid mixes, unless otherwise stated, read in the order: sulfuric acid, nitric acid and water, per cent by weight. The solubilities indicate the percentage weight of the product which is soluble in the solvent mentioned.

I. Slow denitration of a cellulose nitrate containing over 13 per cent nitrogen and insoluble in ether-alcohol.

(*a*) The nitrate used was prepared by the action of an acid mix, 65.80, 24.29, 9.91, for 24 hours at a temperature of 6-8° C. (15 grams of cellulose per 650 grams acid mix). For the slow denitration 150 cc.

[24] *See* Quinan, *J. Am. Chem. Soc.*, 23, 258 (1901).

of acid mix, 38.43, 41.31, 20.26, per 5 grams of product were used. (*b*) Similar results were obtained by the denitration of a sample (13.32 per cent nitrogen) prepared from an acid mix containing 90 grams of sulfuric acid (sp.g. 1.835) and 60 grams of nitric acid (sp.g. 1.483)

TABLE 1.

	Nitrogen Per cent	Solubilities Ether-Alcohol Per cent	Acetone Per cent	Denitration Temperature ° C.	Time Hours
(a) Original	13.43	2.34	100.0	..	..
Final	12.78	99.5	100.0	20	72
(b) Original	13.32	0.0	100.0	..	..
Final	12.96	100.0	100.0	15	60

for two hours at —5 to +5° C. The denitrating acid was 40.14, 43.25, 16.61. Table 1 shows the original and final solubilities together with time and temperature of denitration process.

II. Rapid denitration of an insoluble cellulose nitrate (13+ per cent nitrogen).

The repetition of the denitration of a 13+ sample at a higher temperature and with an acid mix containing a larger percentage of water, resulted in the formation of a product containing about 11.0 per cent nitrogen, completely insoluble in ether-alcohol, and, in part, insoluble in acetone. This last property was taken advantage of to separate the two components and determine their nitrogen content. The preparations of the original cellulose nitrates are: (*a*) see 1(*b*) above, (*b*) acid mix as in (a), time 24 hours, temperature 5-7° C. In both cases the denitrating bath was of the composition, 34.41, 37.17, 28.42. The essential data are shown in Table II; the significance of the results are discussed elsewhere.

TABLE 2.

	Nitrogen Per cent	Solubilities Ether-Alcohol Per cent	Acetone Per cent	Denitration Temperature ° C.	Time Minutes
(a) Original	13.06	2.68	100.0	..	..
Final	11.36	0.0	11.14	40	45
Separation	11.83	0.0	0.0	..	..
	10.93	0.0	100.0	..	..
(b) Original	13.1	5.31	100.0	..	..
Final	9.5	0.93	1.53	55	45

III. The "nitration up" of a soluble cellulose nitrate containing approximately 12.5 per cent nitrogen.

By nitrating a cellulose nitrate of approximately 12.5 per cent nitrogen which was completely soluble in ether-alcohol, with a suitable

acid mix it was possible to procure a new product containing about 13.0 per cent nitrogen, almost completely insoluble in ether-alcohol. It will be sufficient to quote two experiments on samples of nitrogen content 12.40 per cent (prepared by acid mix, 40.14, 43.25, 16.61 for 1 hour at 25° C.) and 12.99 per cent (acid mix 41.03, 44.45, 14.52). The mix used for "nitrating up" was 65.80, 24.29, 9.91. In Table 3 are given the final nitrogen values and solubilities.

TABLE 3.

	Nitrogen Per cent	Solubilities: Ether-Alcohol Per cent	Solubilities: Acetone Per cent	"Nitration Up": Temperature ° C.	"Nitration Up": Time Minutes
(a) Original	12.40	100.0	100.0	..	..
Final	13.13	2.3	100.0	6	10
(b) Original	12.99	99.5	100.0	..	..
Final	13.53	2.67	100.0	6–8	30

IV. The denitration of a soluble cellulose nitrate (12+ per cent nitrogen).

The denitration of an ordinary soluble product of this type was carried out with an acid mix of the composition, 35.87, 38.83, 25.30, at a temperature of 30°-35° C., in less than 30 minutes, to give a partially insoluble product. Three typical experiments (Table 4) show the changes in solubilities.

TABLE 4.

	Nitrogen *Per cent*	Solubilities: Ether-Alcohol *Per cent*	Solubilities: Acetone *Per cent*	Denitration Time *Minutes*
(a) Original	12.55	100.0	100.0	..
Final	10.80	33.5	100.0	30
(b) Original	12.40	100.0	100.0	..
	11.86	96.3	100.0	7
	11.50	79.6	100.0	12
Final	11.25	48.0	100.0	20
(c) Original	12.99	95.5	100.0	..
Final	11.32	47.63	100.0	30

V. The "nitration up" of an insoluble product containing 8.0-9.0 per cent nitrogen.

(*a*) This cellulose nitrate (8.86 per cent nitrogen) was prepared by the action of 260 cc. acid mix, 36.72, 39.78, 23.50 on 10 grams of cotton for 1 hour at 25° C. The composition of the acid used for "nitration up" was 38.43, 41.31, 20.26. Nitrate (*b*) was similarly prepared with a mix, 35.87, 38.83, 25.30, for three hours at 25-27° C. A stronger nitrating acid was used for the higher compound, namely, 63.84, 16.96, 19.20. Table 5 deals with the process of "nitrating up."

TABLE 5.

	Nitrogen Per cent	Solubilities: Ether-Alcohol Per cent	Solubilities: Acetone Per cent	"Nitration Up": Temperature °C.	"Nitration Up": Time Minutes
(a) Original	8.86	0.0	36.3	..	..
	9.52	1.84	58.06	6	2
	9.47	2.2	63.8	..	6
	9.66	17.06	66.6	..	10
	9.71	36.14	81.9	..	25
Final	10.74	100.0	100.0	..	150
(b) Original	8.40	1.54	8.77	..	..
Final	11.10	90.20	99.50	23–24	30

In addition to the above experiments attention was focussed on the behaviour, when peptized in acetone, of two cellulose nitrates differing in nitrogen content, one of them insoluble in ether-alcohol. In all cases so far investigated, it has been impossible to synthesise a new product by this method, the derivatives isolated, by ether-alcohol solubility, possessing a nitrogen content identical with the original esters.

VI. Peptization in acetone.

In this series of experiments equal quantities of two nitrated cottons, one soluble, the other insoluble, in ether-alcohol, were peptized in acetone for varying periods of time (usually 10 grams nitrates per 300 cc. acetone). These were precipitated either by addition of alcohol (95%) followed by water, or, by pouring on cold water. The precipitated product, after thorough drying, was extracted with ether-alcohol; this was best accomplished by repeated centrifuging until the solvent gave no precipitate on addition of water. The ether-alcohol soluble and insoluble specimens were analyzed for nitrogen. (Table 6.)

TABLE 6.

No.	Products Used: Nitrogen Per cent	Products Used: Solubility Ether-Alcohol Per cent	Time of Peptization	Precipitated by:	Nitrogen Content of:[1] Per cent
1........	11.72	100.0	1 hour	Alcohol	s: 11.83, 11.67
	13.1	5.31		& water	i: 13.02, 13.02
2........	12.02	100.0	3 hours	Alcohol	s: 12.25, 12.40
	13.43	2.34		& water	i: 13.3, 13.2
3........	12.02	100.0	7 days	Alcohol	s: 11.7, 11.8
	13.43	2.34		& water	i: 13.22, 13.21
4........	12.02	100.0	3 hours	Water	s: 12.07
	13.43	2.34			i: 13.5
5........	12.38	100.0	24 hours	Water	s: 12.38
	13.28	6.87			i: 13.15
6........	11.0	100.0	1 hour	Water	s: 10.97, 10.9
	13.43	0.0			i: 13.2, 13.1
7........	12.2	100.0	12 hours	Water	s: 11.94, 11.80
	9.45	0.0			i: 9.75, 9.80

[1] s: = soluble; i: = insoluble.

VII. Peptization in ether alcohol.

In a further attempt to synthesise a new product 5 grams of an ether-alcohol-soluble specimen were peptized in ether-alcohol and poured on 5 grams of an ether-alcohol-insoluble nitrate in a round-bottom flask. After standing for two and a half hours the solvent was removed and the residue dried at 80° C. The results from the subsequent separation with ether-alcohol are given in Table 7.

TABLE 7.

	Products Used		
No.	*Nitrogen*	Solubility *Ether-Alcohol*	Nitrogen Content *after Separation*
	Per cent	Per cent	Per cent
1............	11.72	100.0	s: 11.78, 11.34
	8.3	0.0	i: 7.76, 7.93
2............	12.2	100.0	s: 12.09
	13.4	0.0	i: 13.6, 13.39

VIII.

Equal quantities of ether-alcohol-soluble and insoluble specimens were peptized in acetone; to ensure thorough mixing the solution was boiled under a reflux condenser for 90 minutes and allowed to stand at room temperature for 20 hours. The acetone was then removed under diminished pressure and the residue dried at 35° C. After extracting with ether-alcohol the soluble and insoluble portions were analysed as before (Table 8).

TABLE 8.

	Products Used		
No.	Nitrogen	Solubility Ether-Alcohol	Nitrogen Content after Separation
	Per cent	Per cent	Per cent
1............	11.72	100.0	s: 11.77, 11.72
	13.43	0.0	i: 13.23, 13.36
2............	11.0	100.0	s: 10.77, 10.64
	13.43	0.0	i: 13.1, 13.1
3............	12.2	100.0	s: 11.60, 11.56
	9.45	0.0	i: 9.68, 9.72

IX. Variation in time of peptization

Finally, specimens obtained by denitration or "nitration up" were peptized in acetone for varying periods of time. After precipitation, either by addition of alcohol followed by water, or, by pouring on cold water, the solubilities in ether-alcohol were again investigated. These differed from the original only by negligible amounts.

It is the opinion of the author that the slight differences recorded in experiments VI-IX are too small to warrant the assumption that a synthesis of any kind has taken place. The significance of these results is mentioned in a later part of this paper.

Discussion of Results and Conclusions

Until the molecular weight of cellulose or its esters has been determined it will be granted that all views on the subject of the constitution of cellulose nitrates must be empirical. No cellulose nitrate has so far been isolated in the pure state and, owing to the nature of the nitration process, with its ever varying concentration due to the formation of water in the reaction, it seems unlikely that we are much nearer such an isolation. Further, until the configuration of the cellulose molecule has been determined we cannot be certain of the spacial arrangements of the groups forming its esters. It is now recognised by experts in the field of constitutional carbohydrate chemistry that cellulose is the most highly polymerised of the known polysaccharides,[25] a fact which does not tend to simplify the present problem. The advancement of the constitutional formulae for cotton cellulose, although not guaranteed to do more than aim at the simplest structure of the cellulose molecule —no mention being made of the degree of polymerisation—has shown conclusively that glucose is the sole product of hydrolysis of cotton cellulose and that all the glucose residues are identical in structure.[26]

It is already well established that the nitration of cellulose is a continuous reaction, and that products can be isolated containing anything up to about 14 per cent nitrogen. So far, the general tendency has been to assume that the number of cellulose nitrates is very large. If we take the simple anhydroglucose molecule of $C_6H_{10}O_5$ with three available hydroxyl groups, a mononitrate corresponds to 6.77, a di- to 11.13, and a trinitrate to 14.17 per cent nitrogen.

The experimental data submitted above have been interpreted as demonstrating that it is possible, by increased nitration or by denitration, to "nitrate" the *surface* of one of these cellulose esters, the resulting coating determining the solubility of the whole derivative. If this outside coating be of a type soluble in ether-alcohol, it will be possible by this means to peptize the new compound. Again, should this coating be an insoluble material the effect will be a decrease in solubility. We can illustrate the results graphically as follows: (the arrows indicate the direction of the change in nitrogen content as well as the change in solubility):

[25] Irvine and Hirst, *J. Chem. Soc.*, **121**, 1585 (1922); **123**, 518 (1923).
[26] Irvine, *loc. cit.*

A.	B.	C.
	Nitrogen Content (per cent)	
8 + ———→	←——— — 12 + ———→	←slow— 13 +.
	←——————rapid——————	
	Solubility Ether-Alcohol	
Insoluble	Soluble	Insoluble

Figure 1

In the experimental data given in Tables 1 and 2 we have examples of a slow and rapid denitration of a product high in nitrogen content (13.4 per cent), corresponding fairly closely to what most workers claim to be the highest form of cellulose nitrate. It can be considered as a cellulose trinitrate (C_6 . . . basis) with smaller quantities of the mono- and di- varieties. The slow denitration yields a "12.8 per cent nitrogen" product, now completely soluble in ether-alcohol. This can be explained by the hydrolysis on the surface of the trinitrate with subsequent formation of a coating of the soluble B nitrate (Fig. 1), which is capable of peptizing the whole sample in ether-alcohol. Table 2 typifies a very different example; the acid mixes are weak and have resulted in the formation of fairly low nitrogen products (11.3 and 9.5) which are insoluble in ether-alcohol. In the opinion of the author (a) can be explained by the fact that employment of a weak acid mix, at a high temperature, causes further hydrolysis and formation of a coating of almost completely denitrated cellulose or some of the mononitrate. This theory can be substantiated by its low solubility in acetone, its high nitrogen content of 11.3 per cent, and, by the still higher value of the insoluble acetone part, i.e., 11.83 per cent. In 2 (b) the denitration on the surface has been more complete, giving a film of almost denitrated cellulose which cannot be peptized in either solvent.

The B type (12 +) must consist mainly of the denitrated derivative with some of the trinitrate below the surface; this would account for the ease with which the ordinary specimens are soluble in ether-alcohol. By nitrating up on the surface of a "12.40 and 12.99 N" it is easy, in a comparatively short time, to obtain a C type; the increase in nitrogen is only about 0.5-0.6 per cent (Table 3), whereas the degree of peptization in ether-alcohol falls from 100.0 per cent to something approaching 1 or 2 per cent. Again, it seems as if the present theory would account for this in a very satisfactory manner.

In considering the three denitration experiments on the "12+" varieties (Table 4) it is evident that the coating with an insoluble surface has not been so complete. The original products, consisting mainly of the dinitrate, with smaller quantities of the more highly substituted ester, have not fallen much below the nitrogen content required for the

dinitrate, but it will be seen that at 10.80 per cent the product is only 33.5 per cent soluble in ether-alcohol. Here the partial coating of an insoluble mononitrate is evidenced as rendering peptization in ether-alcohol more difficult.

Finally, experiment 5 deals with the "nitration up" of an A form. Judging by the properties of the original substance, it probably consists of unchanged cellulose and a mixture of the mono- and dinitrates. The theory would indicate that by increased nitration on the surface with a soluble dinitrate product the samples are, in (a) easily, and in (b) almost completely, peptized by both acetone and ether-alcohol.

In the light of the foregoing discussion all the data now submitted can be explained satisfactorily, and certainly more simply, on the basis of the existence of three cellulose nitrates. The types A, B, and C (Fig. 1) although non-homogeneous, are those which, in the main, display the properties of these nitrates. The trinitrate C is insoluble in ether-alcohol and soluble in acetone. On slow denitration it yields, with difficulty, an ether-alcohol soluble product (*ca.* 12.8 per cent N), but is readily denitrated to an insoluble specimen with lower nitrogen content (*ca.* 11.0 per cent N). Type B possesses the properties of the dinitrate, easily and completely soluble in acetone and ether-alcohol; it is readily "nitrated up" on the surface to give an ether-alcohol insoluble specimen. The denitration is accompanied with greater difficulty. In discussing the mononitrate the question is a little more complicated. It seems clear that in esters of the type A there is unchanged cellulose present as well as mixtures of the esterification derivatives. At the same time it is not denied that the higher compounds may contain cellulose, but, if they do, only in small quantities in the internal mass and not on the surface as must be the case with the lower products. From the solubility determinations of the A type, described in the experimental part, it is concluded that the mononitrate is soluble in acetone but insoluble in ether-alcohol.

More support would be given to this theory and probably greater light on the more definite interpretation of the number and properties of the nitrates, were it possible to synthesise a new product by means of the mixed nitrate experiments already referred to. The author is confident that this is still possible but, up to the present time no suitable means have been found to accomplish the task. In view of the results obtained with the simple compounds there seems no good reason why this should not take place, but it is certainly accompanied with much more difficulty than was anticipated. As pointed out in the earlier part of this discussion, cellulose is a highly polymerised polysaccharide and it may be that the difficulty is accounted for by this fact. Apparently similar experimental difficulties are being encountered in this laboratory with another colloid problem. Apart from this, however, the theory is a plausible and simple one.

It is of interest to mention here another case in the chemistry of cellulose which can be explained directly by this peptization theory, namely, the question of the oxycelluloses. Here again the tendency has been to complicate this problem by postulating at least three varieties obtained by the action of different oxidisers. The mistake made by many of the workers was in assuming that they had pure oxycellulose and in describing new derivatives because these could be peptized by different solvents. Bancroft [27] clearly points out that there is no evidence for the existence of three different oxycelluloses.

Not only does this theory explain the results now submitted but it clears up many points in the discordant views of the earlier investigators. In demonstration of this let us take the following extract from the literature: [28] "A cotton may be nitrated at a comparatively low temperature, and after nitration is substantially complete so far as nitrogen content of the nitrocotton is concerned, if a sample be withdrawn, and washed to neutrality in the usual manner, while the bulk of the nitrated cotton remains in the nitrating mixture, the temperature of which is considerably elevated, it is possible to produce two nitrocottons, in which the sample first withdrawn is completely soluble in alcohol-ether mixture, while the latter sample is substantially insoluble therein, both containing approximately the same nitrogen content." Here the rise in temperature has been responsible for a denitration or "nitration up" on the surface of the second compound causing a coating of an insoluble product which prevents peptization in ether-alcohol. Both samples may still have "approximately the same nitrogen content."

Again, the example, quoted by De Bruyn, of the soluble and insoluble isomerides (12.7 per cent nitrogen), as well as the results of Mendelejeff,[29] Vieille, Eder, Lunge and Weintraub can be explained and simplified on the basis of the present theory.

Summary

1. An attempt has been made to determine the number and properties of the cellulose nitrates.

2. The theories of the earlier investigators are included in a brief review.

3. Several types of nitrated celluloses have been nitrated and denitrated on the *surface* and their nitrogen content and solubilities in ether-alcohol and acetone determined.

4. The general theory is stated that nitration on the surface with a soluble or insoluble derivative determines the solubility of the resulting product.

[27] *J. Phys. Chem.*, 19, 159 (1915).
[28] Worden, "Technology of Cellulose Esters," Vol. I, Part 3, p. 1721 (1921).
[29] *Monit. scientif.*, 11, 510 (1897).

5. The present results can be explained on the basis of three cellulose nitrates. A few of their properties are discussed.

6. Some applications of the theory to earlier work are briefly dealt with.

In conclusion, the author wishes to express his indebtedness to Professor W. D. Bancroft for suggesting the present problem and for the very helpful criticism he has offered; also, to the Department of Chemistry at Cornell for the privileges of the laboratory which have been so generously extended to him while holding a Commonwealth Fund Fellowship.

Cornell University,
Ithaca, New York.

THE INFLUENCE OF A SECOND LIQUID UPON THE FORMATION OF SOAP GELS

By Harry N. Holmes and Ralph N. Maxson

It is well known that some substances are readily peptized, or dispersed, by mixtures of two liquids neither one of which is a good solvent for the substances in question. Zein,[1] a protein occurring in maize, is insoluble in water and in alcohol, but is readily soluble in a mixture of the two liquids. The maximum solubility is observed in 60 per cent alcohol. Cellulose nitrate dissolves readily in mixtures of ethyl alcohol and ethyl ether, although these liquids taken singly are non-solvents. Numerous similar illustrations might be given.

In a series of attempts to disperse potassium stearate in hot turpentine and to secure a gel on cooling, one of us failed except with one specimen. This and failure with anhydrous soap gave rise to the suspicion that a trace of water greatly aided peptization and gel formation. To test the theory, varying quantities of water were added to weighed portions of anhydrous potassium stearate. These portions were then heated after addition of turpentine and great differences in peptization and gelation noted. The optimum effect was produced when the ratio of water to turpentine was definite but extremely small.

It seemed desirable to investigate quantitatively the influence of relatively small amounts of a second liquid upon the dispersion and gelation of the soaps. Obviously only anhydrous soaps could be used for this study since preliminary experiments indicated the striking influence of traces of water. The stearic acid used probably contained a little palmitic acid as impurity but this did not interfere with a study of water influence.

Preparation of Pure, Anhydrous Soaps

Sodium Stearate.—Stearic acid (300 g.) melting at 49°-50° was added to one liter of water contained in a 16-inch porcelain dish. Sodium carbonate monohydrate was dissolved in one-half liter of water, using fifty per cent in excess of an amount equivalent to the stearic acid. This excess was used to guarantee complete saponification.

[1] Galeotti and Giampalmo, *Kolloid.-Z.*, 3, 118 (1908).

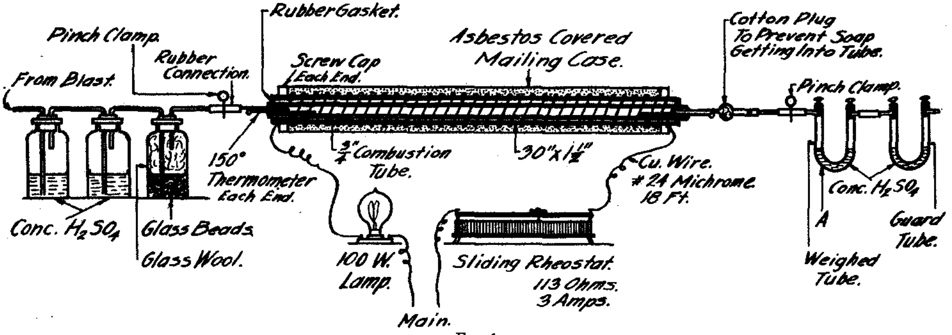

Pinch Clamp.
From Blast.
Rubber Connection.
Rubber Gasket.
Screw Cap Each End.
Asbestos Covered Mailing Case.
Cotton Plug To Prevent Soap Getting Into Tube.
Pinch Clamp.
150° Thermometer Each End.
$\frac{3}{4}$" Combustion Tube.
30" x $1\frac{1}{2}$"
Cu. Wire.
24 Michrome 18 Ft.
Conc. H_2SO_4
Glass Beads.
Glass Wool.
100 W. Lamp.
Main.
Sliding Rheostat. 113 Ohms. 3 Amps.
Conc. H_2SO_4
A
Weighed Tube.
Guard Tube.

Fig. 1.

While the porcelain dish was heated on a water bath the carbonate solution was added slowly from a separatory funnel. A rapidly-rotating stirrer insured efficient mixing but a glass spoon was also employed to break up lumps. After all the carbonate solution had been added, intermittent but vigorous stirring by hand was continued during four hours. When the mass became solid it was broken up with the spoon and one half liter of water stirred in. Finally the soap was dried in thin layers, transferred to sheets of filter paper and dried on the ordinary steam radiators for three days. Of course dust was excluded.

One hundred grams of this air-dried and powdered sodium stearate were boiled for thirty minutes in a pyrex glass flask with 1500 cc. of 95 per cent ethyl alcohol, which dissolved the soap but not the excess carbonate. After further addition of 250 cc. of ethyl alcohol to replace that lost, the hot solution was filtered on a hot water funnel. Solidifying of soap in the stem of the funnel was prevented by intermittent insertion of a hot water heater, a simple device containing the heating unit in a nickel plated metal tube. The filtrate was evaporated to dryness on the steam radiator and the soap flakes obtained finely powdered. This treatment with alcohol removed most of the excess sodium carbonate.

All but a trace of any remaining sodium carbonate was next removed by treatment with absolute alcohol. Seventy grams of the soap dried as above were boiled two hours with 1250 cc. of absolute alcohol in a large pyrex glass flask fitted with a reflux condenser guarded by a calcium chloride tube.

The soap solution was then rapidly filtered through paper into a large pyrex flask and the alcohol distilled off under diminished pressure. After nearly all the alcohol was driven off the soap cake was rapidly broken up with a glass rod, the apparatus reconnected, and evaporation continued. Finally the dry flakes were removed and ground to a powder in dry air and transferred to the electric dryer in Figure 1.

The soap powder contained in the inner tube of the electric dryer was exposed to a slow current of dry air for one hour at an average temperature of 103°. The tube was frequently disconnected, closed with pinch clamps and rotated, thus exposing fresh surfaces. After one hour of this treatment the weighed absorption tube and guard tube were attached to the apparatus and the process continued for forty-five minutes. The absorption tube was then weighed, and replaced for thirty minutes. In no single instance was any evidence of moisture noted. The anhydrous soap powder was then transferred to a dry bottle which was stoppered, sealed with beeswax, and placed in a desiccator.

Sodium Oleate.—This soap was made in the same manner as the sodium stearate. The air-dried material was placed on a Buchner funnel and washed several times with small amounts of cold 95 per cent alcohol. This treatment removed much of the brown coloring matter

derived from the acid. The tendency to form gels with alcohol was much less with this soap.

Potassium Stearate.—The same general procedure was followed in the synthesis of this salt. Due to the liquid character of the soap the stirring was continued for a much longer period than was possible with the sodium soaps.

Potassium Oleate.—This soap was prepared in the same way as described under the synthesis of sodium stearate, using U. S. P. IX. oleic acid. When drying in the electric dryer a small amount of oleic acid condensed in the cold exit end of the tube. This acid was removed by gently heating the exposed end of the tube before attaching the absorption tubes.

Calcium Stearate.—We used the reaction between water solutions at 100° of sodium stearate and an excess of calcium acetate. The latter salt solution was added very slowly while stirring vigorously.

The white precipitate was washed first by decantation, and then collected on a Buchner funnel. The washing was continued until the filtrate showed no test for calcium ions on the addition of ammonium oxalate.

The soap was then washed with 95 per cent alcohol to remove most of the water, and dried. The removal of the last traces of moisture and alcohol was effected in the electric dryer in the manner previously described. The product was a white chalk-like powder, readily dried and weighed.

The Preparation of Soap-Turpentine-Water Gels

The anhydrous soap was weighed as rapidly as possible and transferred to a dry pyrex tube (about 1.5 cm. diameter) which was immediately closed with a dry cork stopper. Distilled water was dropped on the soap from a pipette graduated to 0.01 cc. and calibrated by the Bureau of Standards. After one minute the desired amount of turpentine was added from a calibrated burette and the tube cautiously heated by a microburner. A thermometer was used as a stirring rod and the liquid stirred vigorously until the temperature reached 110°. This temperature was maintained for one minute, then the tube was again closed with the cork stopper and set aside to cool. At the end of three hours it was examined and carefully inverted. The gel of lowest soap concentration that retained its structure under these conditions was then selected as indicating a breaking point.

The dry soaps used in these experiments were stored in dry weighing bottles with tightly fitting ground glass stoppers.

Sodium Stearate Gels.—Sodium stearate, moistened with water, was readily dispersed in hot turpentine. On cooling, firm gels stable from a few hours to several days, depending upon their composition,

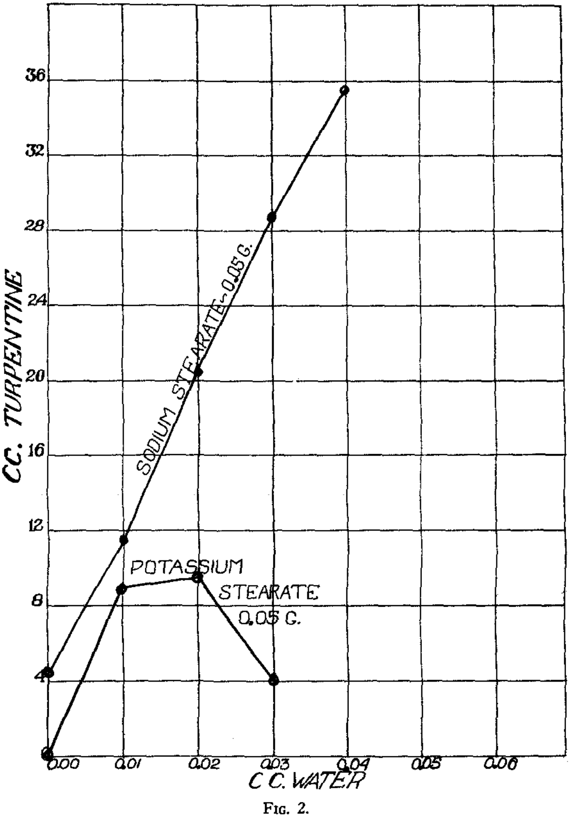


FIG. 2.

were formed. The points on the curve in Figure 2 were obtained by noting the maximum volume of turpentine held in the solid gel when a definite amount of water (for example, 0.01 cc.) was added to 0.05 gm. of anhydrous sodium stearate.

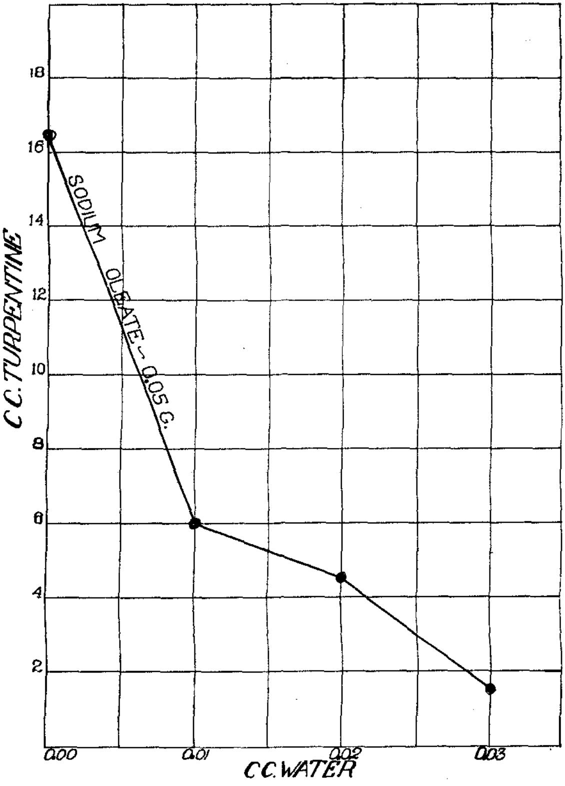


FIG. 3.

It is remarkable that the gel formed with 35.5 cc. of turpentine, 0.04 cc. of water and 0.05 gm. of soap contained only 0.14 of one per cent of solid, 99.86 per cent being turpentine and water. This record has probably not been surpassed by any other gel.

Sodium Oleate Gels.—The influence of water on the formation of turpentine gels of sodium oleate was in sharp contrast with its effect on sodium stearate. The addition of 0.01 cc. of water to 0.05 gm. of the sodium oleate sharply diminished the holding power of this soap towards turpentine. As shown in Figure 3 the ability to form gels practically disappeared when 0.03 cc. of water was present. The contrast between the saturated and the unsaturated soaps was clearly shown.

Potassium Stearate Gels.—Samples of anhydrous potassium stearate prepared in the manner described above were treated according to the procedure adopted in previous experiments. When dispersion in dry turpentine was attempted, it was found that no gels formed at any of the dilutions investigated. When 0.05 gm. of this soap was heated with 35 cc. of anhydrous turpentine the flocculent soap particles formed a milky suspension, but on cooling this gradually subsided without formation of a clear solution or of a gel. This is in striking contrast with the behavior of sodium stearate and sodium oleate. A series of experiments with amounts of dry turpentine varying from 5 cc. to 11 cc. showed no evidence of dispersion, but the addition of a minute amount of water with reheating, yielded gels or distinct evidence of gel structure.

A quantitative investigation of the limits of the holding capacity of this soap for turpentine gave the results shown in Figure 2. As in previous series of experiments the breaking points were located by determining the gel of lowest soap concentration that would withstand inversion without change in structure.

The addition of 0.01 cc. of water and heating to 110° in the manner previously described, caused the formation of typical gels after cooling. These gels were transparent and formed rapidly, in many cases before the tube had cooled to room temperature. In a few minutes small flocks of soap appeared, and after this point was reached turbidity rapidly increased. Syneresis was very pronounced, and the life of the gel structure very brief as compared with that of the sodium soap gels. In many cases the gels lost structure in 10 to 20 minutes, but in a few instances the life extended to four or five hours. In two experiments, due to causes not as yet understood, the gels lasted for 14 hours.

It was observed here, as previously noticed with the other soaps, that the soap particles were at first much swollen, dispersing as the temperature rose above 100°. The addition of 0.02 cc. of water gave no evidence of any very great increase of holding power. It will be noticed that this is very different from the deportment of sodium stearate. The fragile nature of the gels made the location of this point very difficult, but the data were obtained from a large number of experiments and the gels could be reproduced with considerable certainty.

It was noticed during the study of gel formation in this region of the curve that the rate of heating was an important factor. Where the heating was very rapid and gas bubbles were formed in large amount

it was found that the ability to form gels disappeared. A series of experiments with soap systems of much greater concentrations than the critical concentrations shown on the curve, yielded no gels when heated in this manner. When the temperature was raised very gradually, and gas bubbles were evolved very slowly, gels were obtained without difficulty.

When 0.03 cc. of water was added to 0.05 g. of potassium stearate the turpentine holding capacity seemed to be greatly diminished. It was found to be very difficult to obtain consistent results. Loss of water was probably the disturbing factor.

The influence of water as a "helper liquid" in the dispersion and gelation of potassium stearate with turpentine is shown to be significant when 0.01 cc. of water is present. The addition of 0.02 cc. has little further influence but the addition of further amounts of water largely inhibits gel formation. The deportment of the potassium soap in this respect resembles the behavior of sodium oleate.

Potassium Oleate.—The dispersion of anhydrous potassium oleate in hot turpentine was very incomplete. A trace of water aided dispersion in a marked degree. Clear sols were obtained under these conditions, but no gels were obtained upon cooling to room temperature. When the soap concentration was sufficiently increased and the system cooled to zero, gels were obtained at once. These gels were amber color, transparent and had a life of a few days. When the amount of water added to 0.05 g. of soap exceeded 0.01 cc. there was a slight loss in turpentine holding capacity. When 0.03 cc. of water was present gel formation was nearly inhibited.

The Formation of Soap-Turpentine-Oleic Acid Gels

It was considered advisable to study the effect of polar compounds other than water as an aid to the dispersion of soaps in hot turpentine. Oleic acid is a suitable substance for this purpose because it is readily obtained in anhydrous condition and is easily measured volumetrically. The effect of oleic acid upon a lens of "Liquid Petrolatum" has been studied by Harkins and Feldman [1] and it was thought that some similar effect might take place at the soap-turpentine interface.

The acid used was "Acid Oleic Merck; U. S. P. IX" and it was shown to be free from water by testing with calcium carbide and anhydrous copper sulfate.

Sodium Oleate.—An inspection of Figure 4 shows that the addition of relatively small amounts of oleic acid increases the turpentine holding capacity of sodium oleate, quite opposite to the effect produced by water. When as much as 0.03 cc. of the acid is added to 0.05 gm. of the soap the holding capacity is diminished somewhat.

[1] J. Am. Chem. Soc. 44, 2676 (1922).

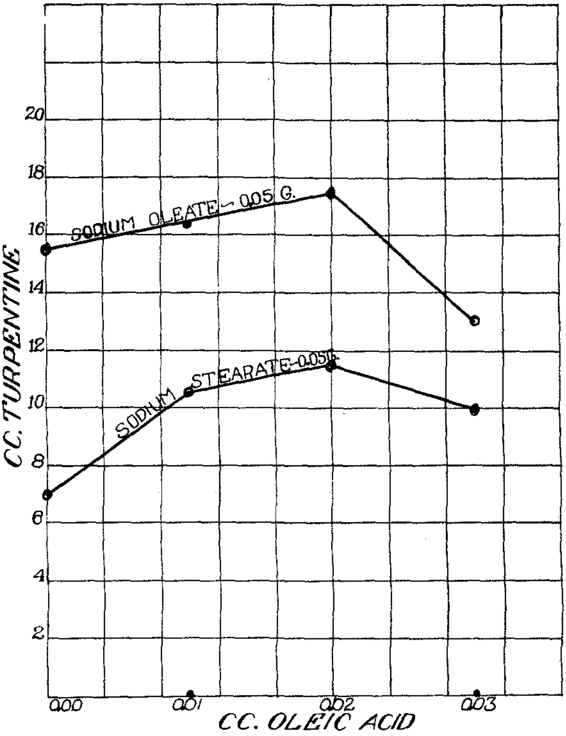


FIG. 4.

Sodium Stearate.—*It is also shown, Figure 5, that relatively small* amounts of oleic acid increase the turpentine holding capacity of sodium stearate while larger amounts diminish the ability to hold turpentine.

Potassium Stearate.—With potassium stearate, using varying amounts of turpentine and oleic acid, no dispersion took place. Some *swelling of the soap was observed but a clear sol was not obtained* and no trace of gel formation was noticed on cooling. This is in pronounced

contrast to the effect produced by water in previous experiments with potassium stearate.

The same specimen of sodium stearate used in the experiments a year earlier was utilized for this work. It will be noticed that the "standard" gel formed at a dilution of 7 cc. of anhydrous turpentine (without a helping liquid) although in the previous work any dilution above 4.5 cc. failed to produce a stable gel. This change in holding capacity is probably due to adsorption of water (a helping liquid for this system) although the material had been stored in containers fitted with well ground stoppers.

A series of parallel experiments with the system sodium stearate-turpentine-stearic acid showed that 0.01 cc. of melted stearic acid slightly decreased the turpentine holding capacity of 0.05 g. of sodium stearate while addition of 0.05 cc. of the acid completely inhibited gel formation.

The Formation of Soap-Paraffin Oil-Oleic Acid Gels

Sodium Stearate Gels.—Sodium stearate is readily dispersed at 200° in paraffin oil (density 0.8499 at 20°). On cooling, beautiful clear gels are formed.

When 0.1 cc. of oleic acid was added to 0.05 gm. of the soap, firm gels were always formed if the oil concentration did not exceed a critical value. Transparent sols were first formed, then as gel structure progressed, turbidity became very pronounced. When the concentration of oleic acid exceeded 0.1 cc. gel formation was absolutely inhibited. Transparent sols were obtained but no gel structure was ever observed. Swollen particles forming a "sludge" were always precipitated on cooling.

Inspection of Figure 5 shows that anhydrous sodium stearate can be dispersed in paraffin oil, forming firm transparent gels, but that the addition of a trace of oleic acid diminished the oil holding capacity of the soap in an astonishing degree. Further additions of the acid absolutely inhibit gel formation.

When stearic acid was used instead of oleic acid as the "helper" liquid the paraffin oil holding capacity of sodium stearate was not affected. However, the stability of the gels was affected to an astonishing degree. The gels were transparent at first but in thirty minutes became turbid and after a few hours lost their gel structure.

Potassium Oleate.—Paraffin oil gels of potassium oleate were unsatisfactory, obtained only at high soap concentrations. Dispersion at 200° was incomplete and the gels formed on cooling were very turbid. The addition of small amounts of stearic acid did not change the paraffin oil holding capacity in any significant degree.

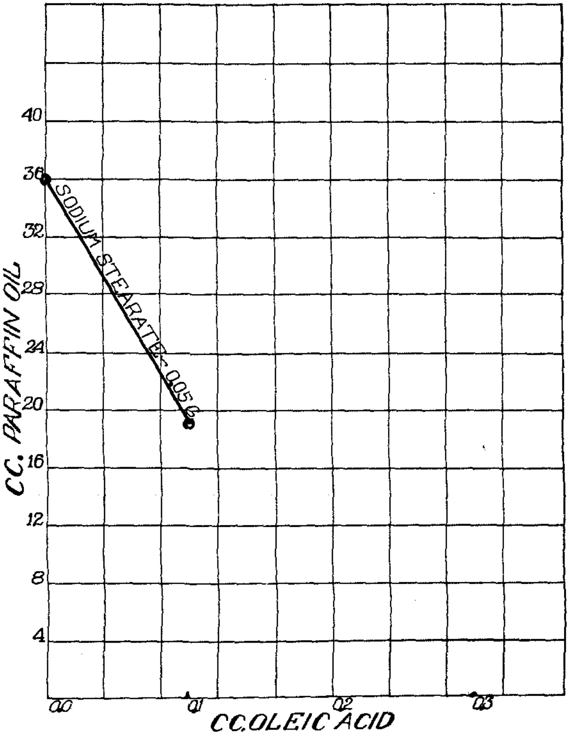


Fig. 5.

Calcium Stearate Gels.—Dispersion seemed to be complete in paraffin oil at 250° but practically all the soap settled out on cooling. No good gel formation was noticed at any concentration. Dispersion in the hot oil was retarded by the presence of the water and gel formation was inhibited. Relatively small amounts of oleic acid or stearic acid added to the soap and oil yielded gels on cooling. The average life of these gels, formed at the concentrations used, was about thirty-six

hours. The gels were opaque at higher concentrations, and translucent at lower concentrations, breaking rather suddenly, without excessive preliminary syneresis.

Further addition of oleic acid (0.2 cc.) did not show significant increase in oil holding capacity. It was noticed, however, that increased concentration of stearic acid greatly increased the oil holding capacity. When 0.3 cc. of this acid was present gel formation at lower

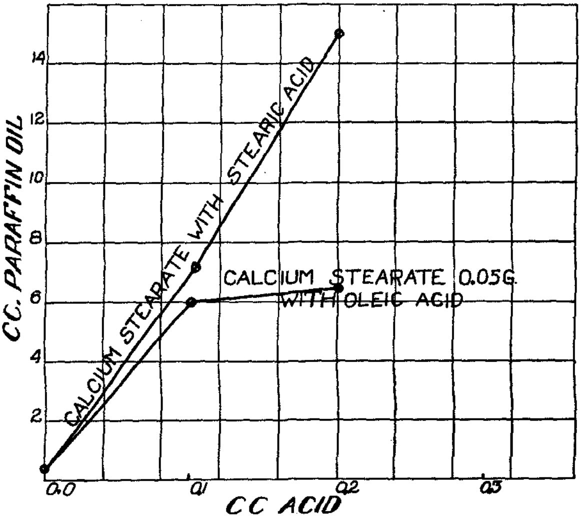


FIG. 6.

concentrations was noted, but the life of the gels was shortened to a few hours.

It is supposed that a certain amount of water is necessary to obtain stability in commercial cup greases, containing calcium stearate. These results would indicate that slight excess of stearic or oleic acids is a more important factor. Of course the presence of other soaps such as the stearate or oleate of sodium must make the situation more complicated. Investigation of this system will be continued.

THE FORMATION OF SOAP-BENZENE-FATTY ACID GELS

Oleic Acid.—It has been shown above that relativeley small amounts of oleic acid slightly increase the holding power of anhydrous sodium stearate towards turpentine (Fig. 6). Similarly it was found that relatively small amounts of oleic acid aid dispersion in hot benzene. When the weight of sodium stearate was increased to 0.1 gm. dispersion

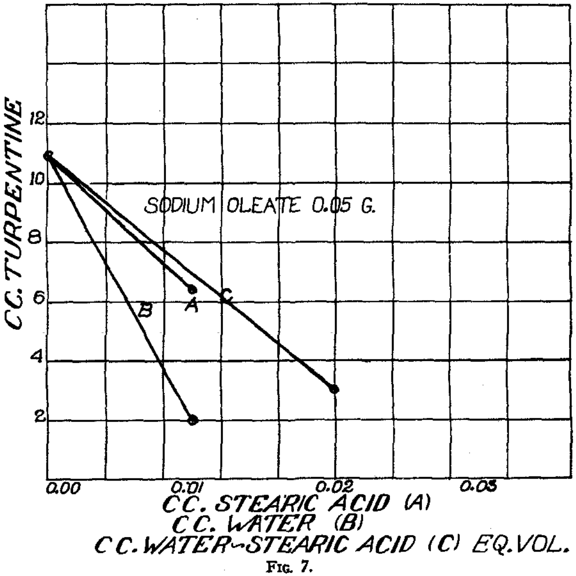


FIG. 7.

was complete, if 0.1 to 0.2 cc. of the acid was present, and distinct traces of gel were formed on cooling. In the absence of oleic acid dispersion was incomplete and most of the soap settled out upon cooling. No gels, firm enough to stand inversion, were obtained at any concentration.

Stearic Acid.—As previously noted sodium stearate is incompletely dispersed in hot anhydrous benzene and most of the soap is precipitated on cooling. However, when 0.1 cc. of stearic acid is added to 0.05 gm.

of sodium stearate in 4 cc. of benzene a gel forms at once on heating and cooling. The gel was at first transparent but in the course of a few minutes became cloudy. The nuclei gradually grew and had a distinctly crystalline appearance. The life of this gel was three hours.

It is remarkable that no gels formed when more than 0.1 cc. of stearic acid was present. As stated before, no gels formed in the absence of stearic acid.

The Formation of Sodium Oleate-Turpentine Gels as Affected by Presence of Both Water and Stearic Acid

The final experiments on gel formation were made with a two-year-old sample of sodium oleate with which the original results could not quite be duplicated.

When 0.05 gm. of this sodium oleate was heated with turpentine (Fig. 7) in the presence of both water and stearic acid (0.01 cc. each), the dispersion was good and, on cooling, firm gels resulted with the use of as much as 3 cc. of turpentine but not with as much as 4 cc. In comparison it is to be noted that 0.05 gm. of this soap held only 2 cc. of turpentine as a gel when aided by 0.01 cc. of water while it held 6.5 cc. of turpentine when aided by 0.01 cc. of stearic acid. This intermediate point merits further investigation.

Oberlin College, Oberlin, Ohio.
The University of Kentucky, Lexington.

COLLOIDS IN THE ELECTRODEPOSITION OF METALS [1]

By William Blum [2]

I. Introduction

The extensive literature upon the effects of colloids in metal deposition was fully summarized in the excellent paper on this subject by Sand [3] in 1922. Recently it has been announced that this bibliography has been amplified and brought up to date by W. E. Hughes for a British Colloid Symposium. As this revision will be published shortly it will obviate the necessity of including an extensive bibliography in this paper. Instead, an effort will be made to present a bird's-eye view of the present status of the subject, and to indicate the most promising directions for future research. Only incidental references will be made to the literature, and these chiefly to articles published in the past five years.

In order to consider this subject adequately, it is necessary to take into account, at least for purposes of comparison, the effects in electrodeposition of addition agents in general, whether they be colloidal or not. There is no entirely satisfactory simple definition of an addition agent. In general it may be described as a substance which is added to a solution used in electrodeposition, in order to produce an effect upon the structure of the deposit, although it does not materially change the conductivity or the concentration of metal ions or of hydrogen ions in the solution. As will be pointed out later, most of the effects of addition agents are so closely associated with changes in the cathode polarization that we might tentatively refer to addition agents as "polarization agents." Such a definition might include those few addition agents that decrease the polarization, as well as the much larger number that increase it. Even then, however, it would be necessary to exclude those substances such as acids and salts that produce large changes in conductivity and metal-ion or hydrogen-ion concentration, along with changes in polarization. In general the term addition agent suggests the use of very low concentrations, such as a few parts per million of glue in copper refining baths. There is, however, no sharp distinction, as some substances such as glucose and

[1] Published by permission of the Director of the Bureau of Standards, Department of Commerce, Washington, D. C.
[2] Chemist, U. S. Bureau of Standards.
[3] "The Role of Colloids in Electrolytic Metal Deposition," H. J. S. Sand, *Fourth Report on Colloid Chemistry*—Brit. Assn. Adv. Science, 1922.

glycerol have been used in fairly high concentrations. In most cases, however, true colloidal agents are used (beneficially) only in low concentrations, sometimes as low as 1 milligram per liter. Unless otherwise stated, it will be assumed that the colloids referred to in connection with metal deposition are positiveley charged and hence migrate toward the cathode.

One of the reasons for including at least some discussion of addition agents that are not apparently colloidal, is the suggestion that has been frequently made, that their effects are due to the presence of colloidal impurities in them, or to the formation or stabilization of colloids because of their presence. Before discussing this question, it might be well to summarize the effects in electrodeposition of addition agents, especially of those that are colloidal.

II. Effects of Colloids

1. Crystal Structure.—The most obvious effects of addition agents, which effects are usually responsible for their intentional use, are the changes produced in the structure of the electrodeposited metals. Such changes may be exhibited by the macroscopic as well as the microscopic appearance of the metals. Most addition agents produce smoother deposits, and reduce the tendency for the formation of "trees" or projections upon the surface, which are otherwise likely to form at points of high current density, such as edges and corners. In consequence, addition agents are frequently employed, e.g., in copper refining, to permit the use of higher average current densities than could otherwise be applied. It is noteworthy, however, that a few addition agents that are beneficial in certain solutions, actually increase the tendency toward treeing in other solutions and sometimes cause characteristic growths. In most cases an excess of the addition agent promotes the formation of "burnt" or spongy deposits.

In general the increased smoothness of the deposit is accompanied by a decrease in the size of the individual crystals. This decrease is often so marked that it has at times given rise to the designation of such deposits as "amorphous." Actually, however, in the light of modern x-ray analysis there is no justification for this application of that term. It is not sufficient to designate a deposit as "fine-grained," as the type of crystal may be even more significant than its size. Thus "fibrous" deposits which are unlikely to form with addition agents present, might be referred to as fine grained, although of course one dimension is relatively large. Most addition agents tend to cause the formation of deposits with a "broken" or haphazard structure, in which the individual crystals are usually small and show no favored orientation. Apparently the addition agent has decreased the tendency for the

growth of existing crystals and increased that for the formation of new crystals.

2. Composition of Deposit.—Numerous examples have been reported in which the colloid, or at least some material derived from it, e.g. of an organic nature, is found in the electrodeposit, in amounts varying from mere traces to a per cent or more. On the other hand there are a few cases in which none of the addition agent or of its possible decomposition products can be detected in the deposit. As will be shown later, some of these apparent exceptions have been adequately explained.

Besides entering into the deposit, an addition agent may change the proportions of metal deposited in an alloy. Thus in brass plating, substances such as phenol, which are added as "brighteners," may change at least slightly the ratio of copper and zinc in the deposit. If they do so, it is probably by producing a selective effect on the polarization curves for the deposition of the respective metals.

3. Throwing Power.—In addition to changing the structure of the deposited metal, addition agents usually improve the "throwing-power," i.e. they tend to produce a more uniform distribution of metal upon a cathode of irregular shape. Thus it was found [4] that in an acidified copper sulfate solution, which without any addition agent had a throwing power of 9.6 per cent (as measured in a box with a 5 : 1 ratio) the addition of 10 grams per liter of dextrin increased the throwing power to 12.2 per cent, and the addition of 0.2 gram per liter of gelatin, to 18.0 per cent. Haring [5] found that dextrin produced a similar though relatively smaller increase in throwing power in nickel solutions. To some extent the tendency toward the formation of smoother deposits with addition agents is associated with this improvement in throwing power. Granted a certain degree of roughness from any cause in the deposit at an initial stage, good throwing power will decrease the tendency of projecting points to grow more rapidly than the deposit in the depressions.

As both throwing power and crystal structure have been shown [6] to depend upon the cathode polarization, the conductivity and the cathode efficiency, it is interesting to determine which of these factors is most affected by the presence of the addition agent.

4. Cathode Polarization.—It has been long recognized that in the presence of addition agents, especially those that are colloidal, the cathode polarization is appreciably increased. In his discussion of this subject, Sand [7] attempts to differentiate between "transfer resistance" and "polarization." It would take us too far afield to discuss the evi-

[4] H. E. Haring and W. Blum, *Trans. Am. Electrochem. Soc.*, **44**, 313 (1923).
[5] *Trans. Am. Electrochem. Soc.*, **46**, 107 (1924).
[6] Haring and Blum, *Trans. Am. Electrochem. Soc.*, **44**, 313 (1923); Blum and Rawdon, *ibid.*, **44**, 397 (1923).
[7] *Loc. cit.*

dence for and against the existence of a transfer resistance at the cathode. In most cases the term has been discussed by Newberry and others in connection with gas evolution, rather than with metal deposition. It is interesting to note that H. D. Holler [8] found by two new methods that when a gas is evolved in electrolysis, there is some sort of resistance at the cathode surface, for which he suggested the term "boundary resistance," without attempting to explain its nature or cause. In a few experiments with copper deposition, however, he found no evidence of any such resistance.

The term polarization as used in this paper in connection with metal deposition will be defined as the difference between the static or equilibrium potential of the deposited metal in that solution, and its "dynamic" potential, i.e. the potential when the current is passing with a given current density. It will be assumed, at least for present purposes, that the polarization is equal to the difference between (*a*) the potential drop from a non-polarized electrode of that metal through a given path of solution to the cathode when current is flowing and (*b*) the potential drop through an equal path between two non-polarized electrodes [9] with the same current flowing. In other words, it is the increase in potential drop above that corresponding to the IR drop through that same path of solution, and represents a corresponding increase in the energy consumption. Regardless of whether this increased voltage is due entirely to counter emf or to some new IR drop introduced as a result of cathode discharge, it is apparently effective in determining the throwing power and the crystal structure.

There is considerable evidence that the addition of colloids such as gelatin in small amounts to acid copper or zinc solutions, produces little or no effect upon the static or equilibrium potential. Such substances do however very materially change the dynamic potential (making it more negative), i.e. they increase the cathode polarization. This change in polarization at first increases with an increase in colloid concentration, and then tends to reach a maximum which, however, is not sharply defined. Thus in acid copper sulfate solutions Haring [10] and Rouse and Aubel [11] found a maximum increase in cathode polarization of about 0.10 volt at 1.5 amperes per square decimeter, when the gelatin concentration was from 15 to 20 mg. per liter. In normal zinc sulfate solutions, Isgarischew and Titow [12] obtained the maximum polarization with 250 mg. per liter of gelatin, while Rabald [13] observed a maximum with only 50 mg. per liter of gelatin. Such apparent contradictions serve to emphasize the difficulty of correlating conflicting statements on addition agents. Many of the published data must be consid-

[8] *Bureau of Standards Scienctific Paper* 504 (1924).
[9] H. E. Haring, *Trans. Am. Electrochem. Soc.*, 49, 417 (1926).
[10] *Ibid.*, 49, 417 (1926).
[11] *Ibid.*, 51, preprint (1927).
[12] *Kolloidchem. Beihefte*, 14, 25 (1921).
[13] *Z. Elektrochem.*, 32, 289 (1926).

ered as qualitative rather than quantitative, owing to the failure (sometimes for then adequate reasons) to define the exact properties and concentrations of the addition agent, the composition and pH of the solution, the conditions of operation, and the method of measurement or observation. The time is ripe for an exhaustive study of a few typical addition agents, making use of the suggestions derived from the somewhat casual observations on the great variety of substances mentioned in the literature.

One of the practical objections to the commercial use of addition agents has been the difficulty of determining and controlling their very low concentrations by analytical methods. Recently it has been shown by Haring that within the limits in which addition agents such as gelatin are generally used, it is possible to determine their effective (if not their actual) concentration by simple polarization measurements. This method of control has now been adopted in several copper and lead refining plants.

There are at least a few cases in which addition agents which produce a much finer crystal structure, decrease the cathode polarization. It was observed by Haring[14] that carbon disulfide, which is commonly used as a "brightener" in silver cyanide solutions (and in fact was one of the first addition agents used in commercial plating) decreases the cathode polarization. This subject is now under investigation by Dr. S. C. Langdon and his associates at Northwestern University. Haring also found that sodium thiosulfate, which is used commercially as a "brightener" in cyanide copper baths, decreases the cathode polarization. It may be only a coincidence that both of these exceptional addition agents are sulfur compounds. Such apparent exceptions illustrate the present difficulty of making any comprehensive generalizations on the effects of addition agents on polarization, until more detailed data are available.

The common positively charged colloids employed in acid solutions also increase the anode polarization, but to a less extent than that at the cathode. This effect, while interesting, is usually less significant in electrodeposition than the influence at the cathode. Colloids that are negatively charged tend to migrate toward the anode, and to produce there the greatest polarization.

5. Conductivity.—The fact that the presence of addition agents increases the total voltage required in a given cell to produce a certain current density, has often led to the erroneous conclusion that such substances decrease the conductivity of the bath. Actually it has been shown that this voltage increase is due almost entirely to a change in anode and cathode polarization, and that the effects on the conductivity, if any, are so small as to be negligible. Recently Skowronski and

[14] *Trans. Am. Electrochem. Soc.*, **49**, 417 (1926).

Reinoso [15] have shown that even as much as 1 gram per liter of glue, i.e., 300 times as much as is used in copper refining, changes the conductivity less than one part in a thousand, if at all.

6. Cathode Efficiency.—Colloids may either increase or decrease the metal cathode efficiency, and no simple rule can be given. Usually the cathode efficiency is a resultant of the respective tendencies for metal deposition and hydrogen evolution. Such tendencies, at least for the separate processes, may be expressed in terms of the cathode polarization curves for metal deposition and hydrogen discharge on that metal surface. As previously indicated, colloids are likely to increase the metal cathode polarization. If this occurs without changing the hydrogen polarization, the cathode efficiency will be decreased, i.e., the evolution of hydrogen will be made relatively easier.

It has been long known, however, that many colloids increase the hydrogen polarization or overvoltage. If this increase is greater than that of the metal polarization, the metal cathode efficiency will be increased. Obviously, much further study will be required to determine which of these conditions exists for any given metal, solution, and colloid; and still more to predict the behavior under other conditions.

Tainton [16] also found that gelatin in a zinc solution lowers the contact angle of hydrogen bubbles and thus facilitates their detachment from the cathode. The practical cathode efficiency is thereby increased, as there is a tendency for re-solution of zinc wherever hydrogen bubbles cling permanently.

III. Mechanism of the Effects of Colloids

From the preceding brief summary of some of the effects of colloids it is evident that their influence is more closely associated with conditions at or near the cathode surface than with those in the body of the solution. As a matter of fact this state of affairs applies almost equally to all factors which affecet the structure or distribution of metal deposits. In order to understand fully any electrolytic process, it is necessary to know what is taking place (*a*) in the metal cathode itself, (*b*) in the thin film of solution adjacent to it, which will be referred to as the "cathode film," and (*c*) at the actual interface between metal and solution. But it is just here that our knowledge is woefully lacking. The mechanism of conduction of current in metals involves the location and movement of the electrons with respect to the atomic centers in the space lattices, on which x-ray analysis throws no light, and on which the new physics is still speculating. Much is known about the migration of ions and colloidal particles during electrolysis, but the concentration or activity of ions in the body of the solution is

[15] *Trans. Am. Electrochem. Soc.*, **51**, preprint (1927).
[16] *Trans. Am. Electrochem. Soc.*, **41**, 389 (1922).

still a matter of uncertainty, and even less is known about such concentrations in the immediate vicinity of the cathode. There is no general agreement as to how and where the electrons from the cathode combine with the positively charged ions to form neutral metal atoms. With the theories of even the simplest electrolytic processes in so unsettled a state, it is not surprising that we have no adequate explanation of the effect of colloids.

Merely in order to have some definite basis for considering these effects, the theory of Blum and Rawdon[17] will be employed, without implying that equally plausible explanations might not be based on other suggested theories. According to this hypothesis the union of one or more electrons with a positively charged ion takes place on the cathode surface, at a point determined both by the orientation of the metal atoms on the cathode surface, and by the effective concentration (i.e., the activity) of the metal ions in the cathode film. The latter concentration is approximately measured by the dynamic potential of the cathode. When this ion concentration is high the cathode polarization will be low, and conditions will be favorable for the growth of existing crystals. Conversely, when the metal-ion concentration is low and the cathode polarization high, the conditions are less favorable for crystal growth and more favorable for formation of new crystals. This assumption is based on the well known fact that small crystals of metal have a higher solution pressure and a more negative potential than large crystals and that hence more negative potentials will be required for the production of fine crystals.

According to this theory any change in conditions which increases cathode polarization must tend to make changes in the type of crystal structure in the order from fibrous to conical, to broken and finally to spongy or powdery deposits. Just such changes in structure, especially to the latter two types, are most frequently produced by colloids. It seems reasonable therefore to assume that at least the principal effects of colloids on crystal structure are associated with the increase in cathode polarization which they produce.

The problem then resolves itself into "why and how do colloids increase cathode polarization?" It is generally admitted that in order to be effective, especially in very low concentrations, the colloids must migrate toward the cathode, i.e. they must be positively charged. Of course, if the colloid is in relatively high concentration in the body of solution, e.g., 1 gram per liter or more, it is not necessary to assume migration to the cathode in order to have there an appreciable concentration, which may then exist there even if the colloid tends to migrate away from the cathode.

Although the importance of pH in electrodeposition, especially of metals such as nickel, zinc and iron, is now generally recognized, it

[17] *Trans. Am. Electrochem. Soc.*, **44**, 397 (1923).

was only recently that Frölich [18] called attention to the relation of the pH of the solution to the migration of the colloids during electrodeposition. If a colloid such as gelatin has an isoelectric point of pH = 4.7, we may expect that in a solution with a lower pH it will migrate toward the cathode and have an influence there, but that in a solution with a higher pH it will move toward the anode. Such an explanation may be equally valid whether we assume with Frölich that the protein is amphoteric or whether we consider that its charge is due to adsorbed ions, e.g., hydrogen or hydroxyl ions. It is not easy to subject this theory to a crucial test, owing to the frequent difficulty of measuring the pH of metal salt solutions containing proteins, and especially the uncertainty as to the pH of the cathode film. In nickel and zinc solutions this is undoubtedly higher than the pH of the body of solution. Hence it is possible, as Frölich has suggested, for the colloid to migrate *toward* but not *to* the cathode surface, as its charge is reversed when it reaches the (relatively) alkaline film at the cathode. In such a case we might expect it to exert an effect on the polarization, but not be appreciably included in the deposit. Frölich has found that although gelatin is included in copper deposited from acid solutions containing it, it is not found in zinc deposits from acid solutions. This difference he attributes to the fact that although the gelatin migrates toward the cathode in each case, it reaches it only in the copper solution in which the pH of the cathode film is less than that of the rest of the solution; and not in the zinc solution, in which the cathode film is relatively alkaline.

It has also been frequently suggested, most recently by Fuseya and Murata,[19] that the colloid may form complex ions with the metal and that such ions may migrate to and be discharged at the cathode, thus accounting for the inclusion of organic matter in the deposits. If this were generally true, we would expect a more marked effect upon the metal-ion concentration and therefore upon the static potential, than has usually been observed, even with fairly high concentrations of colloids.

Recent experiments of Fuseya and his students [20] are of interest in this connection because they show conclusively that such crystalloidal additions as metaphosphoric acid, citric acid, tartaric acid and glycocoll, produce finer grained copper or silver deposits, which contain appreciable amounts of the added compound. They found complex ions in these solutions, but no colloidal particles could be detected. Other crystalloidal substances such as sucrose, mannite and resorcinol, that have no appreciable effect on the structure or weight of the deposit, do not form complex ions. Whether colloids such as proteins that are effective addition agents also produce complex ions remains to be

[18] *Trans. Am. Electrochem. Soc.*, 46, 67 (1924).
[19] *Trans. Am. Electrochem. Soc.*, 50 235 (1926).
[20] *Trans. Am. Electrochem. Soc.*, 50, 235 (1926), and 51, preprint (1927).

seen. The above authors did not measure the cathode polarizations, and hence it is not known whether the changes they observed in the static potentials were also accompanied by even larger changes in the dynamic potentials. If so, their results would not necessarily detract from the great importance of polarization in connection with addition agents.

It is noteworthy that in their second paper they report that the effects of glycocoll in copper sulfate solutions upon the appearance and weight of the deposits and upon the formation of complex ions, are almost completely eliminated when the sulfuric acid content of the solution is normal. This at least indicates that the acidity has an important effect upon crystalloidal as well as upon colloidal addition agents.

The above conclusion, that organic non-colloidal substances can be included in an electrodeposited metal, is consistent with the observation of Frölich[21] that carbonaceous substances of unknown constitution may be co-deposited with iron or nickel from solutions containing salts of organic acids such as oxalates, or through which gases such as acetylene are being passed. No colloids could be detected in such solutions. Frölich attributed such inclusions to the catalytic effect of iron or nickel upon gas reactions at the cathode. These observations are of interest chiefly as indicating that colloids are not necessary concomitants of inclusions. As the cathode potentials were not measured in these experiments, it is impossible to state whether such "gas reactions" were accompanied by an increase in the polarization.

Whatever the form in which the colloid (or other addition agent) exists, it must in most cases migrate to the cathode, and there increase the cathode polarization, in order to affect the structure. This increase in polarization may be brought about by any means that decreases the metal-ion concentration in the cathode film. As a result of metal deposition the metal-ion concentration must always be at least slightly lower in the cathode film than in the rest of the solution. The agencies that contribute to the replenishment of metal ions at the cathode are dissociation, migration, diffusion and convection. Of these the last two are likely to be affected by the presence of the colloid. The natural convection that occurs as a result of the change in density of the solution produced by the deposition of metal from it, is especially affected. The presence of even low concentrations of colloids in or near the cathode film may cause sufficient changes in the viscosity and the surface tension to reduce materially such convection currents and thus increase the polarization. It may be noted that such an effect may be produced by a colloid that approaches the cathode surface regardless of whether it reaches it or not, as the most rapidly ascending stream is likely to be at an appreciable though still small distance from the cathode surface.

[21] *Trans. Am. Electrochem. Soc.*, **46**, 87 (1924).

Granted that the colloid in relatively high concentration actually reaches the cathode surface, it may become included in the cathode deposit either by (1) co-discharge of colloid particles and metal ions, (2) discharge of complex ions containing the metal and the colloid, (3) adsorption of colloid upon the face of the metal deposit, or (4) mechanical inclusion in the deposit. It is difficult from the meager data available to suggest the relative probabilities of these processes, especially since, as shown by Frölich, a colloid may affect the structure of the deposit without any detectable amount of the colloid entering into the metal; and as shown by Fuseya, organic materials may enter the deposit from solutions containing no colloid. If the colloid enters the metal, we may have interference with the normal growth of crystals and hence an increased tendency for the formation of new crystals and of finer grained deposits. In such a case the presence of the colloid in the solution reduces the available metal-ion supply, and its presence on the cathode decreases the number of exposed points on the metal upon which the ions can be discharged. Both factors would result in an increased polarization.

The specific effects of colloids, and especially the tendency of certain ones to produce characteristic growths, may possibly be associated with their selective adsorption on different crystal faces, to which C. H. Desch [22] has called attention. The fact that a given colloid is not equally effective in different salts of the same metal, may be due to differences in the initial metal-ion concentrations and in the polarizations produced without colloids in the different solutions, rather than to any direct effects of the anions upon the colloid or upon the deposited metal. Very little is definitely known regarding the relative polarization changes produced by various addition agents, or in different solutions. Such measurements would at least throw light on their observed behavior.

Recent X-ray studies [23] have confirmed the above general theory at least to the extent that they have shown that lead deposits produced from solutions containing colloids are finer grained. On the other hand such deposits showed evidence of preferred orientation, which observation is not consistent with the earlier studies of Frölich and Clark [24] on nickel, iron and copper, for which a decrease in crystal size was always accompanied by a reduced tendency toward preferred orientation. This discrepancy is still to be explained.

The recent success of S. E. Sheppard in showing by moving pictures the migration and deposition of colloidal rubber particles, suggests the interesting possibility that the movement of colloidal particles in metal deposition, and their relation to the crystal growth on the cathode might be similarly studied.

[22] In his address, "Growth of Metallic Crystals," delivered to the American Institute of Mining and Metallurgical Engineers, Feb. 1927.
[23] Frölich, Clark, and Aborn. *Trans. Am. Electrochem. Soc.*, **49**, 369 (1926).
[24] *Z. Elektrochem.*, **31**, 655 (1925).

Frequent references have been made to the possible effects of inorganic colloids in electrodeposition. One of the most common illustrations is the well known effect of aluminum salts in producing brighter zinc deposits from acid baths. Frölich [25] concluded that such effects are due partly to colloidal aluminum hydroxide at or near the cathode surface. As aluminum hydroxide starts to precipitate at a pH of from 3 to 4, it must undoubtedly tend to form during zinc deposition in the cathode film, the pH of which approaches 6.2. Thompson [26] however, has suggested that the effect of an aluminum salt is due principally to its buffer action, as it prevents the cathode film from becoming less acid than about pH 5 so long as any appreciable amount of the aluminum salt remains to be hydrolyzed. It thus retards any precipitation of zinc hydroxide at the cathode. Thompson was unable to detect aluminum in any form in the zinc deposits from such solutions. His experience indicates the possibility that a colloid such as aluminum hydroxide may produce brighter zinc not because it enters into the deposit, but because by its precipitation it prevents zinc hydroxide from being formed and possibly included in the deposit. It is well known that many "burnt" deposits of metals contain basic salts or hydroxides, which may also be present in even merely dull deposits. In such cases the bright deposits may be the purest metal. Certainly the brightest nickel, zinc and iron deposits are produced from solutions (containing no added colloids), when the pH is relatively low, i.e. when there is the least tendency to form basic precipitates.

One of the most interesting inorganic colloids is "chromium chromate," which is always present in chromic acid plating baths. Haring [27] originally considered that its presence was beneficial, and suggested that it served to control the pH. More recently he has shown [28] that it is not only unnecessary, but may be actually detrimental. At least there is no evidence that it enters into, or directly affects the structure of the deposited chromium, although it probably always exists in the cathode film regardless of its concentration in the body of solution.

Many of the addition agents that are not themselves colloidal contain at least traces of colloids. Thus commercial glucose, a very common addition agent, contains appreciable amounts of dextrin, and in fact pure dextrose has no measurable effect on the polarization or throwing power in copper deposition. It is at least possible that crystalloidal substances which form no detectable colloids in solutions of metal salts may give rise to colloids in the cathode film, where the hydrogen-ion concentration and other conditions may be appreciably different from those in the body of solution. And even if the complex ions containing metals and crystalloids never reach colloidal dimensions, they are prob-

[25] *Trans. Am. Electrochem. Soc.*, **49**, 395 (1925).
[26] *Trans. Am. Electrochem. Soc.*, **50**, 193 (1926).
[27] *Chem. Met. Eng.*, **32**, 692 (1925).
[28] Bureau of Standards Tech. Paper 346 (1927).

ably sufficiently large to form a natural transition from simple ions to true colloids. Microscopic or X-ray observations of deposits containing these "crystalloidal" addition agents may ultimately indicate the state of aggregation in which they are present in the metal.

IV. Conclusions

The preceding discussion might almost better have been entitled "Unsolved problems on the effects of colloids in electrodeposition," as it shows so clearly the inadequacy of existing knowledge as a basis for any comprehensive theory of the subject. The progress in the past five years is, however, far from discouraging. New methods have been applied and old ones have been improved. Qualitative observations have been succeeded by definite quantitative masurements of such important factors as acidity, polarization, and throwing power. The X-ray is being applied to the problem with promising results, which, however, require more extended study for their complete interpretation. The new concepts of physics and physical chemistry have given at least an inkling of what happens at an interface between a metal and solution during electrolysis. It is, therefore, reasonable to expect that within the next ten years this subject of colloids in electrodeposition, which has always been shrouded in an air of mystery and empiricism, will take its rightful place as one of the most important phases of electrochemistry.

U. S. Bureau of Standards,
Washington, D. C.

COLLOIDAL FERRIC HYDRATE IN MOLDING SAND [1]

The Influence of a Surface Film of Hydrated Iron Oxide on the Bond in Sand-Clay-Water Systems.

By Clyde C. DeWitt and George Granger Brown

1. Introduction

The production of cast metal articles has always been one of the fundamental industries. During the last decade the increase in the manufacture of castings, both ferrous and non-ferrous, has been so great as to threaten the exhaustion of natural deposits of molding sand which are necessary to the production of good metal castings.

A molding sand has been defined by Littlefield [2] as any material which when moist can be formed into a mold from which usable metal castings may be made. This definition includes all combinations of sand and clay or other material, and it implies all desirable qualities that a molding sand must have, the two most important of which are bond, so that the mold may have sufficient strength to support the metal while being poured, and permeability to gases, so that the gases may readily escape giving a sound casting free from blow holes.

The cause of permeability is reasonably well understood and satisfactory tests for this property have been developed, adopted and are in constant use.

Of the cause of bond in molding sand very little definite information is available. It has been thought that the presence of iron oxide had something to do with the bond,[3] but there is also some evidence that is contradictory.[4] Little agreement is found concerning the origin and condition of the iron oxide even among those who consider iron oxide important in giving bond to a sand.

Condit [4] states that the hydrated iron oxide films on sand and clay particles are formed by precipitation of iron salts from surface water. "Surface waters charged with organic acids readily dissolve iron. As these waters percolate downward the iron is precipitated between the

[1] *Part of a dissertation submitted in partial fulfillment of the requirements for the degree* of Doctor of Philosophy in the University of Michigan by C. C. DeWitt.

Acknowledgment is made to the State Geological Department for the grant making possible this investigation.

[2] Littlefield, *Ill. State Geol. Survey*, Bull. No. 50, 1925, p. 20.

[3] King and Schlichter, *U. S. Geol. Survey*, 19th Annual Report (1899); Boswell, *Engineering*, 108, 418-20; 464-66 (1916); *Foundry*, 47, 593 (1919); *Trans. Am. Foundrymen's Assoc.*, 27, 305 (1918); Hanley and Simonds, *Foundry*, 48 772-4 (1920).

[4] Condit, *Trans. Am. Foundrymen's Assoc.*, 21, 21-27 (1912); Moldenke, "Principles of Iron Founding," McGraw-Hill Book Co., N. Y., 1917.

sand grains. For this reason the grains of most molding sands are thickly coated with limonite."

In direct contrast to Condit's views, Gordon [5] accounts for the presence of colloidal gel coatings on silicate particles as formed by decomposition of the sand grains themselves. Whitney [6] also considers that the soil colloids are derived from the sand particles which become hydrolyzed not by being precipitated from solution but by molecules of water bombarding the soil particles when they have reached a diameter of 0.0001 mm.

Boswell [7] reports the beneficial effects of iron oxide as a binder in the British red sands as follows:

"The chief natural bonds in molding sands are ferric hydroxide and clay substance (silicate of alumina, fine micas, etc.). These like many of the artificial bonds in common use, are colloidal bodies. The adsorptive power of clay, in the matter of both gases and solutions increases, according to Senfft, with the limonitic content. J. Van Bemelen found as long ago as 1878 that the amount of 'hydrate water' of ferric oxide was variable and accidental. When just dry at 15° C. the compound is able to take up over six molecules of water per molecule of ferric oxide. One of the most marked characteristics of the best sands is their extraordinary power of taking up considerable quantities of water without really becoming wet. The following figures, for example, are those of hygroscopit water (liberated at 110° C.) contained in molding sands (some of them moist but none wet) as collected in the field.

	Per cent	
Cornish Red	11.6	
Erith strone	10.2	
Belgian Yellow	6.6	partly dried
Wolverhampton	13.5	
Kiddermaster	8.0	

"Another important desideratum of good molding sands, possibly connected with the colloidal character of the bond, is that they should not 'go dead,' that is, dehydrate too readily after metal has been cast in them. Iron oxide readily hydrates again, unlike clay which may be 'porcelainized' by heat.

"The distrihution of the bond in naturally bonded sands is ideal. Each grain of quartz is coated with a thin pellicle of ferric hydroxide or ferruginous clay. Water skins cannot hold on to clean quartz, but each coated grain assumes the skin of water, which with its neighbors constitutes the enormously strong 'green bond' of the sand.

"It is noteworthy that in the West European sand the higher the percentage of ferric hydroxide the greater is the transverse strength in the sands. In the case of the sand from south Africa containing 4.81

[5] Colloid Symposium Monograph, Vol. 3, p. 114 (1924).
[6] *Science*, 54, 656 (1921).
[7] *Engineering*, 108, 418-20, 464-66 (1916).

per cent of ferric hydroxide, the molds produced were of extraordinary strength and toughness."

Hanley and Simonds[8] express their belief that the majority of the well bonded molding sands of this country owe their bonding qualities to the presence of colloidal hydrated ferric oxide as follows:

"In the study of many sands surprising results are obtained in connection with the effect of iron oxide on the bonding property. . . . Just what composes the 'clay substance' (bond) in molding sand is not generally understood, and the following analyses of the bonding material after it is separated from the sand may serve to clear up this point.

	New Jersey Sand Per cent	Ohio Sand Per cent	New York Sand Per cent
Silica	41.70	33.65	38.88
Iron Oxide	14.27	28.88	24.67
Alumina	25.40	18.15	22.50

In another article Hanley and Simonds[9] state, "Ferric Oxide practically always is present as an impurity in natural molding sands, and its percentages as shown by chemical analyses, often give a good indication of the amount of the bond in the sand. Ordinarily common sand without bonding properties will show an iron oxide content of 5 to 6 per cent, whereas in molding sand the ferric oxide may run from 3½ to 15 per cent. The importance of the iron content of a sand is not generally recognized, but from experience with a large number of sands with varying iron content, it has been proven that a relation exists between the percentage of iron oxide and the bonding quality. The iron content alone is not sufficient in some cases, for a sand containing five or six per cent may have almost no bonding property or it may have a fairly good bond."

Bean[10] considers iron oxide detrimental in molding sand even when present in small amounts. His views are criticized by Shaw.[11]

Moldenke[12] considers iron oxide bad, but admits to a limited degree its beneficial action on bond as follows:

"A further noticeable point in a number of so called 'red' sands is a very high percentage of iron oxide, this rising to 7.5 per cent in some English sands. In one case near Vienna a sand is used with over 11 per cent iron oxide, and again another sand with nearly 12 per cent of lime. Both of these ingredients are bad, as they are fluxing, but it is interesting to note that a moderate percentage of iron oxide, if distributed over the surfaces of the quartz crystals as a stain and encrustation is not objectionable to a serious extent, as it serves as a base to hold the clay more firmly to the otherwise smooth surfaces of the grains, particularly if they are well rounded."

[8] *Foundry*, **48**, 722-4 (1920).
[9] *Foundry*, **48**, 743 (1920).
[10] *Trans. Am. Foundrymen's Assoc.*, **26**, 419 (1917).
[11] *Trans. Eng. Ceram. Soc.*, **13** (1913-14).
[12] "Principles of Iron Founding," McGraw-Hill, N. Y., 1917.

Boswell[13] notes that molding sands fall into two classes, naturally bonded sands which contain ferric hydroxide or certain silicates, and high silica sands which must be bonded artificially with such substances as *sugar, dextrin, molasses, oil,* or *sulfite lees.* He[14] states that the ferruginous bond improves the life of the sand and assists in the production of a smooth sound surface to the casting particularly in the case of steel. It should be noted that this view is practically the opposite of that held by Moldenke and Bean.

Kennedy[15] calls attention to the fact that all attempts to produce artificial molding sands with the same bond as natural sand have been unsuccessful because of improper distribution of clay around the grains, giving a sand lacking in durability. He suggests that these failures are due to a lack of knowledge of the properties of iron oxide as a binder, and of ability to coat sand grains with colloidal hydrated iron oxide. Although it has been recognized for some time that colloidal ferric oxide films might have an important influence on the bond strength of sands, no quantitative data have been presented to show the effect of such films, or to account for the bond in molding sand in terms of such films.

This paper reports quantitative data showing the relation of colloidal ferric oxide adsorbed on the sand grains and on the clay bonding material to the strength of bond in the molding sand, and the successful preparation of synthetic molding sand obtained in the course of work done on Michigan sands for the Michigan Geological Survey. The effect of colloidal iron oxide on the hond of molding sands has been determined by analytical methods on natural sands; and by synthetic methods successfully reproducing the bond of natural molding sand by the proper combination of clean unbonded sand or silica, kaolin, and ferric hydrosol.

2. Testing Methods

Five four-hundred-gram portions of the dried sand were weighed out and each mixed in either a tin or an aluminum dish with enough distilled water measured from a burette so that the samples would contain approximately 4, 6, 8, 10, 12 per cent of water respectively. In some cases when only four samples were taken, the same range of percentage water content was covered at slightly different intervals. As soon as the samples were mixed they were put into clean Mason jars provided with rubbers and sealed. The samples were allowed to stand for at least twenty-four hours before being tested.

At the end of twenty-four hours the jars were opened and samples prepared for permeability and bond tests.

[13] *Foundry,* 47, 148-50 (1919).
[14] Boswell, *Jour. Inst. Metals,* 22, 292 (1919).
[15] "A Summary of the Literature on Molding Sand," *Am. Foundrymen's Assoc.,* 1922.

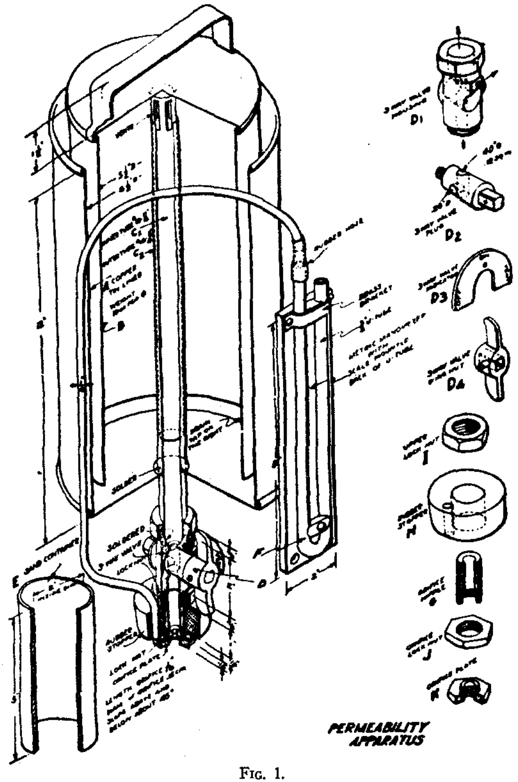


FIG. 1.

Permeability.—The test used for permeability is that adopted by the American Foundrymen's Association. The permeability apparatus [16] is shown in Figure 1. Tank *A* is made of copper, tin lined and is provided with a vertical air outlet tube coming through the bottom of the same. When in use this tank is partly filled with water. A stopcock

[16] *Trans. Am. Foundrymen's Assoc.*, Vol. 31, pp. 708-721.

is provided on the side of the tank *A* at the bottom, to drain off the water when the apparatus is not in use. Bell *B* has a vertical tube, *C-1*, which slides inside outlet tube *C-2*, in tank *A*. Near the top of this tube are several vents to permit the air to be forced out of bell *B*. A three way valve *D* is attached to the lower end of the outlet tube from tank *A*. The opening in the valve should not be too small, preferably not less than 0.12 sq. inch (3 sq. mm.) so as to permit the air to pass through freely. The parts of this valve are shown as D_1 to D_4 inclusive. A valve indicator, D_5, is provided, marked "on," "off," and "vent," to show when valve is in position to let air from bell *B* through sand container *E*;

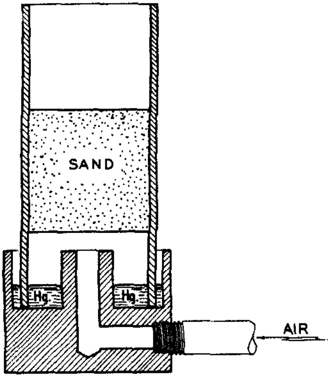


FIG. 2.

to shut off flow of air from bell, or to permit air to enter by pass while raising the bell. An orifice plate *K* for use in rapid work is screwed into the lower end of the nipple *G*. The rubber stopper *H* fits into a steel shell the other end of which is closed with the exception of a ⅛ inch projecting nipple. This nipple is connected to the inlet of the device for holding the compressed sand cylinder while the air from the bell is passing through it.

The device shown in Figure 2, used to hold the cylinder containing the sample of sand while the permeability test is being made, is a block of cast iron in which an annular groove 1 inch inside diameter, 3 inches outside diameter, 1½ inches deep is cut. The hub of the annular groove is drilled centrally to within half an inch of the bottom of the piece. At an elevation of one side of the piece sufficient to leave a small portion

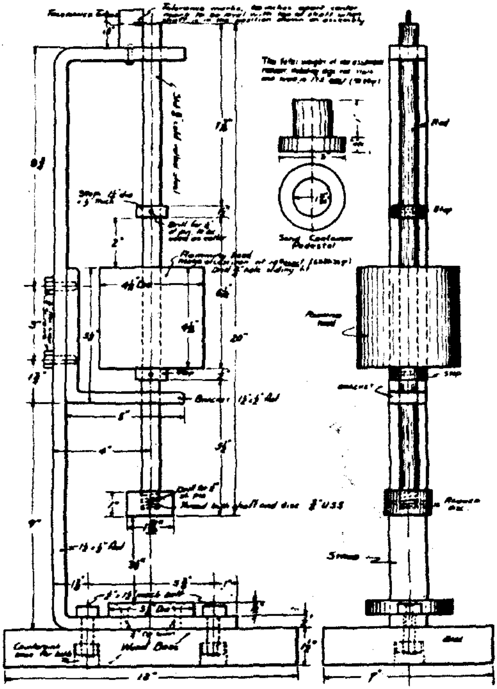


FIG. 3.

of the centrally drilled hole as well, a hole is drilled and tapped for a ⅛ inch pipe nipple. A ⅛ inch nipple screwed tightly into the hole serves as the gas inlet. A short length of heavy walled rubber tube is used to connect this nipple with that on the bottom of the steel shell attached to rubber stopper *H*. A steel cylinder 2 inches internal diameter 2¼ inches outside diameter 5 inches long is used to form the sample. The cylinder containing the formed sample is placed end on in the annular groove, which is filled half full with mercury to form a seal that prevents the escape of air coming from the gasometer.

As the bell B sinks in tank A it drives the air into the outlet pipe *C-1*, Figure 1, through the valve D and through the container E, a steel cylinder 2 inches internal diameter which is set in the device used to hold the sand cylinder when the permeability test is being made.

The pressure of this air is read on manometer F. Since the pressure recorded on the manometer depends on the weight of the bell B and on

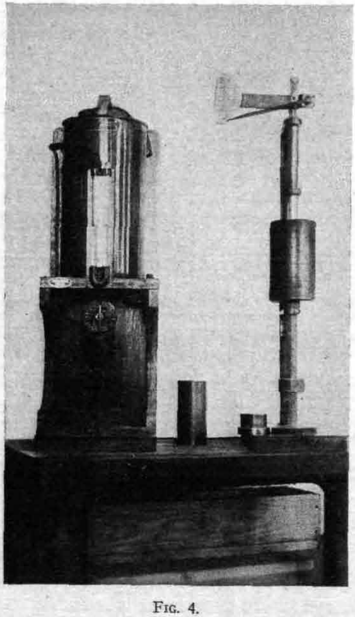


FIG. 4.

its cross sectional area a weight is provided which can be placed on top of B, sufficient to increase the manometer pressure readings to 10 centimeters of water.

The detailed drawing of the sand rammer for the permeability test is shown in Figure 3. It consists of a steel rod supported by two guides. A steel disc is attached to the lower end of the rod, and has a sliding

fit in the sand container *E*. A cast iron weight weighing 14 lbs. (6350.36 grams), slides on the rod, its movement being regulated by two stops. The distance between these stops is sufficient to permit a 2 inch movement of the rammer head. A pedestal is provided on which the sand container *E* rests while sand is being placed in it; and while the ramming operation is being performed. The pedestal is shown in Figure 4.

In place of the tolerance gage, used in the A.F.A. apparatus, shown in the drawing at the top of the guide rod frame, an indicator, consisting of a brass frame on which is pivoted a light beam carrying a knife edge contact one inch from one end was used. A stop on the pivoted side of the beam prevents the beam from jumping out of position. A scale at the end of the indicator beam is calibrated between 1.75 inches and 2.25 inches by hundredths of inches by placing Johannsen gage blocks of the proper size on the pedestal underneath the rammer. The face of the rammer is caused to rest on the gage blocks, the indicator beam is swung over so that the knife edge touches the top of the steel guide rod and the point at the tip of the beam marked on the scale with a short line for each .01 inch.

Figure 4 shows the photograph of the permeability apparatus and rammer.

In preparing the specimens, container *E* of the permeability apparatus was placed on its pedestal, filled almost level with the sand and placed in position under the rammer head. The rammer head and guide rod were allowed to rest momentarily on the sand while the weight was lifted to contact with the upper stop and allowed to fall. The ramming operation was repeated a total of three times on each sample, after which with the weight and guide rod in position, the indicating beam was swung over until the knife edge bearing came in contact with the top of the guide rod. Thus the height of the rammed specimen was read and recorded.

Tank *A* of the gasometer was filled with water to within 4¾ inches of the top. Valve *D* was opened to "Vent" and bell *B* raised until the zero mark was a little above the top edge of *A*. Valve *D* was turned "off." The sample and its container *E* were placed end on in the device having the annular groove half filled with mercury, and Valve *D* turned "on." The time taken for the bell to sink from the zero mark on the side of the bell to the 2000 mark on the bell was noted by means of a stopwatch, and recorded. The difference in levels of the water manometer *F* was recorded. The permeability of the sand was calculated by the following equation:

$$\text{Permeability} = \frac{(\text{cc. of air}) \times (\text{cm. height of specimen})}{(\text{gms. pressure}) \times (\text{area in sq. cm. of specimen}) \times (\text{time in minutes})}$$

Bond or Strength.—The indication of the bond of molding sand has been accomplished by several methods: by the dye adsorption method and by certain physical tests such as failure of a prepared sample in transverse, tensile, compression, or shear.

For some time it has been recognized that the dye adsorption test as applied to molding sands is not an exact index of the amount or quality of the bonding material. Gordon [17] and his collaborators have shown that for certain types of dyes a true chemical equilibrium exists where certain dyes are used to determine the soil colloids. An unpublished work of Crane [18] confirms this conclusion of Gordon. In general the dye adsorption test is not considered a satisfactory indication of bond strength among foundrymen and scientific investigators such as Moldenke,[19] Hanley and Simonds,[20] Doty,[21] Condit,[22] Harrington,[23] Bradfield.[24]

Considerable difference of opinion is expressed by various investigators on the relative values of the various physical tests in indicating the strength of the bond in molding sand. The difference of opinion seems to be about equal to the number of types of machines brought forth by the sponsors of these tests. Adams [25] has made a careful survey of the different types of testing machines that have been described in the literature up to 1926. Inasmuch as the compression test seemed to afford one of the best known tests of bond strength, a machine for testing the bond strength of molding sands by failure in compression was constructed as shown in Figures 5 and 6. The principle upon which the machine is built is that of a simply supported beam, between whose supports a weight is caused to travel at a constant rate.

This testing machine offers the following advantages:

1. No initial loading of sample.
2. Freedom from impact fuses.
3. Constant rate of loading.
4. Automatic operation, stopping and indication of breaking load.
5. Accurate and sensitive to less than one gram.

The rammer used in preparing specimens for compression tests (Figure 7) is somewhat similar to that used in the permeability tests, being an adaptation of that described by Dietert.[26] It consists of a steel rod supported by a steel frame. The guides of this steel frame are drilled to give the steel rod a sliding fit. A cast iron head weighing exactly seven pounds slides on the rod. Stops pinned to the steel rod

[17] "Colloid Symposium Monograph," Vol. 2, p. 114 (1924).
[18] Private Communication to the authors through Prof. Chas. H. Behre of Geology Dept. of Univ. of Cincinnati (1926).
[19] *Op. cit.*
[20] *Trans. Am. Foundrymen's Assoc.*, 28, 741 (1920); *Foundry*, 48, 772, 867, 921 (1920).
[21] *Trans. Am. Foundrymen's Assoc.*, 30, 796-822 (1921).
[22] *Ibid.*, 21, 19-52 (1913).
[23] Harrington, Wright, Macomb, *ibid.*, 30, 782-796 (1922).
[24] *J. Am. Chem. Soc.*, 45, 2669 (1923).
[25] *Trans. Am. Foundrymen's Assoc.*, Preprint No. 26-1 (1926).
[26] *Trans. Am. Foundrymen's Assoc.*, 33, 721-757 (1925).

regulate the movement of this head to 1.95 inches. The sand is placed in a cast iron cylindrical mold 1⅛ inches internal diameter on a steel pedestal.

The frame supporting the steel rod is secured to a piece of cast iron 21 by 18 by 3 inches, both flat sides of which are smoothly machined. An indicator consisting of a brass frame on which is pivoted a light beam carrying a knife edge point one inch from the pivoted end is used to measure accurately the height of the rammed sample.

The scale at the end of the indicator beam is calibrated from 1.75 inches to 2.20 inches by hundreds of inches using Johansen gage blocks.

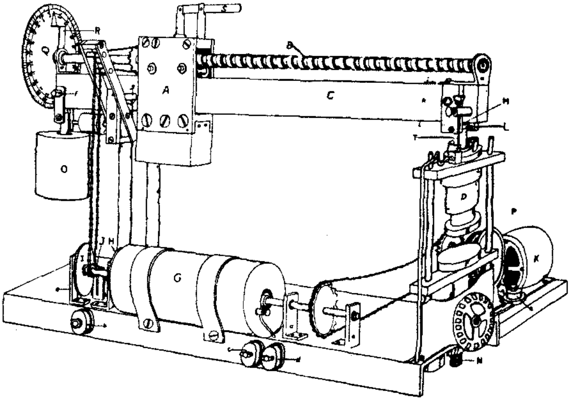


FIG. 5.

The cast iron collar of the pedestal of the ramming device was adjusted so that the cylinder resting on it would contain enough sand to form a sample about two inches high by 1⅛ inch diameter (about 38-44 gms.). The sand was transferred to the forming cylinder on the pedestal and the weight of the steel guide rod and rammer head allowed to rest momentarily on the top of the sand while the weight was being raised by hand to the upper stop pin. As the weight came in contact with the upper pin it was allowed to fall.

This was done three times for each sample, care was taken that during the ramming operation the face of the rammer was always in contact with the face of the sample.

Directly after ramming, with the rammer face still resting on the

sample, the beam of the indicator was swung into position so that the knife edge bearing came in contact with the top of the guide rod and the height of the sample read to the nearest 0.005 inches from the scale and recorded.

The samples was rammed from one end only. The reason for this was to eliminate any possibility of error in preparation, that might be due to any small misalignment of the sand cylinder top and bottom rammer which might occur if the sand were rammed from both ends causing the three to bind and stick or otherwise absorb the kinetic energy which should have gone into compressing the sand sample to the re-

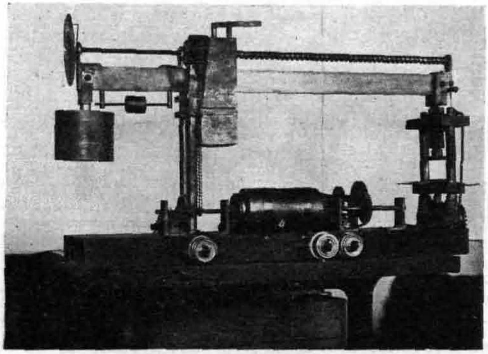


FIG. 6.

quired dimensions. Preliminary work showed this precaution to be a refinement necessary for consistent results. Reversing the ends of the samples rammed from one end only in the testing machine showed no difference in breaking strength.

The samples were stripped from the cylindrical mold by lifting the mold off the pedestal and pressing the sample out of the mold on a long steel pedestal or column of like diameter. The sample was grasped between the thumb and forefingers and the excess sand blown off each end.

The sample was then placed on the movable face plate *F* of the compression machine, Figure 5. The motor having been started and switches (*b*, *c*, *d*, *e*) closed, the position of the sample adjusted to bring it almost into contact with the upper surface *E* by means of the hand wheel

raising and lowering *N*. Switch *d* was snapped off setting the weight in motion. When the sample was broken the weight was automatically stopped indicating the breaking load by its position. The crushing plates were carefully wiped free of sand, and opened by turning the hand wheel. Some broken parts of the sample that fell were caught

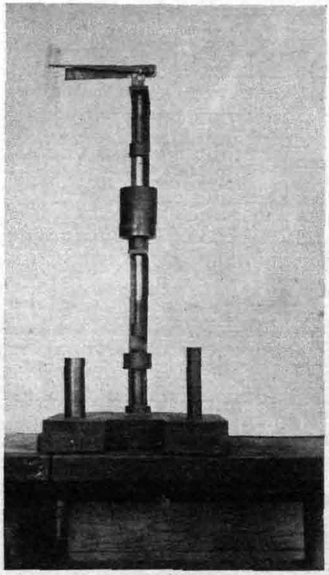


FIG. 7.

on a clean piece of paper placed below the front end of the machine; the sand which came in contact with nothing other than metal or paper or wooden table top was returned to an individual container provided for that particular sand.

The cylindrical mold was carefully cleaned by drawing a clean cloth through it and any sand that might be near the pedestal or on it was removed after each determination. When a completed series of tests

on one sample had been run any scattered sand on the machine and the table where the ramming had been done was carefully brushed up and returned to the container.

At least three and in most cases five or more individual checks were made on each sample. The simple relation suggested by Hansen [27] that the breaking strength of a cylindrical sample of constant diameter and constant water content is inversely proportional to its height, can be applied through a narrow range in height as from 1.80 to 2.05 inches with an error of less than 2 per cent in most cases. This allowed the direct computation of the breaking strength to a height of 1.95 inches, the height at which the reported strengths are computed. The method of computation involved the multiplication of each breaking strength by the height of the sample broken, averaging the numbers so obtained and dividing their sum by 1.95. This method made it unnecessary to have all test specimens the same height.

Determination of Water Content.—The water content of the sample of sand contained in each jar was determined on a whole sample of 38-80 grams of sand prepared in the usual manner. The sample was placed in a weighing bottle, weighed, dried for 24 hours at 105-110° C., cooled and reweighed, the difference in weight was regarded as the water content. The water content of sand samples after testing varied slightly, not more than 0.1 per cent, from the moisture content of samples taken from the bottle. The difference was within the experimental error so that it really made little difference whether tbe sample for moisture content was taken directly from the bottle or from the fragments of a test specimen.

Water Still.—At the outset it was thought desirable to have available large quantities of very pure water to eliminate the uncertainty in colloidal systems for using impure water. A continuous column still of relatively high capacity was designed and built to supply this need. This equipment comprised two still bodies with steam coils, two columns interconnected and two condensers one at the top of each column as shown in Figure 8.

The water is vaporized in the first still body. The vapor travels upward through the packing of the first tower, a portion of it is refluxed down the tower and is discarded through a trap at the bottom, thus effecting a separation of the less volatile impurities. The remainder of the vapor travels across to the second tower where it is condensed, flows down through tower packing, meeting as it comes down an upward current of steam generated from pure distilled water in the second still body, part of which escapes through an orifice in the top of the second tower carrying off the more volatile impurities. At the base of the

[27] *Trans. Am. Foundrymen's Assoc.*, 32, 57-97 (1924).

second tower some of the water is tapped off through a trap, the balance going into the still body to be revaporized to furnish the steam for scrubbing the water coming down the column free of more volatile impurities and gases.

All parts of the still coming in contact with the water or water vapor are made of block tin. The packing in the columns is made of

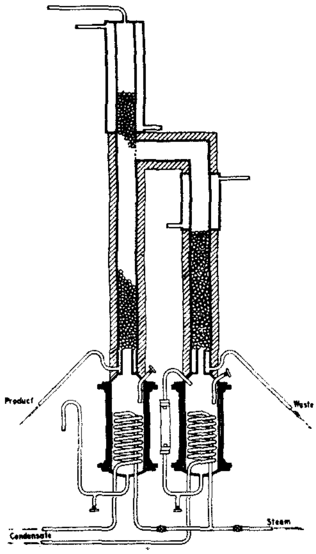


FIG. 8.

one-fortieth inch sheet block tin cut and formed into Raschig rings three-fourths inch diameter by three-fourths inch thick.

3. ANALYSIS OF NATURAL MOLDING SAND

For the purpose of investigating the cause of bond in natural molding sand a sample of fresh Albany molding sand was adopted for testing and analysis. The Albany sand is a more durable sand than can be

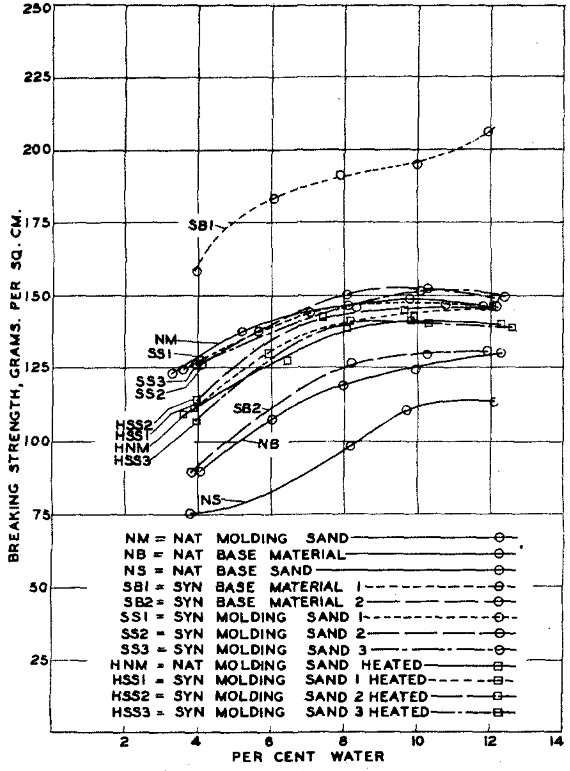


Fig. 9.

obtained in Michigan and is representative of sands containing the most satisfactory bond.

Natural Molding Sand.—The natural Albany molding sand was carefully dried in air, and at 105-110° C., then thoroughly mixed and quartered to yield a sample of 2,000 grams which was preserved in a glass jar.

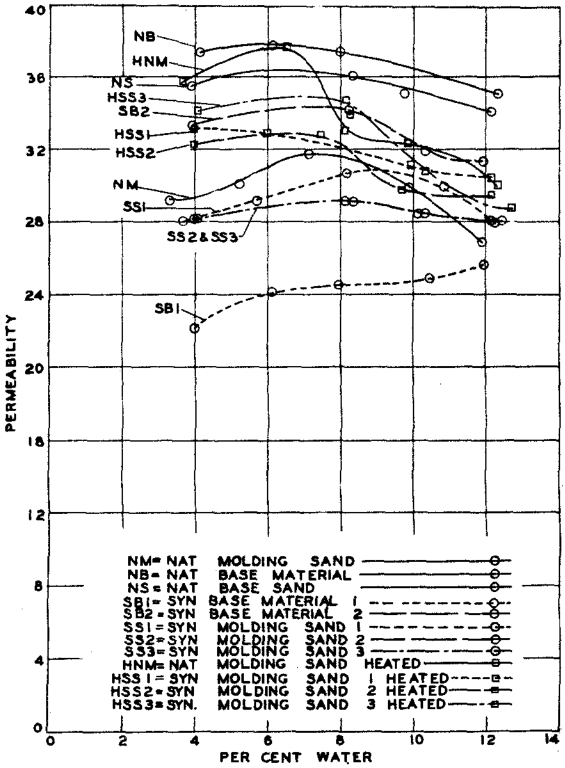


FIG. 10.

This sand was tested for bond and permeability by the methods described and with the results given in Table 1. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability plotted as a function of moisture content in Figure 10.

TABLE 1.—PROPERTIES OF THE NATURAL MOLDING SAND.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.3	532	1.760	122.9	29.2
5.2	576	1.906	137.6	30.1
7.14	624	2.064	144.15	31.8
9.82	646	2.137	148.2	29.9
11.83	634	2.098	146.4	27.0

Natural Base-Material.—The natural base-material was prepared from the natural molding sand hy removing all of the clay silt, or loam surrounding the individual sand grains, which could be removed by washing with water.

The so-called "clay substance" was removed from the natural Albany molding sand by repeated washing and shaking with tepid distilled water. Some 40 lbs. of sand were distributed in clean quart Mason jars one-half pound of sand to each jar. Twenty jars of sand were treated at one time. Each jar of sand was filled with distilled water to about two inches from the top. The jar was tightly stoppered, thoroughly shaken, and allowed to settle until the last one of the jars had been so treated. The water was then siphoned out of the first jar, care being taken to have the end of the three-sixteenths-inch rubber tube siphon at least three-fourths inch above the level of the sand layer that had settled out. The water suspension of silt, etc., siphoned off was caught in an enameled pan and transferred to a steam jacketed Duriron kettle. This operation was repeated on each of the jars continuously for about two weeks, at the end of which time the water above the sand could be seen to be perfectly clear. In the meanwhile all the washings and silt had been evaporated to dryness, collected and weighed. It constituted about 13 per cent of the original dried sample. A screen analysis indicated that all of this material passed through a 270-mesh sieve.

The natural *base-material* of the molding sand was washed out of the jars into an enameled container, excess water decanted through a filter paper on a Buchner funnel, the sand so caught returned to the container. The natural base-material was air dried, then dried for one hour at 105° C. and mixed for testing.

SCREEN ANALYSIS.

Mesh	Per cent on
50	0.028
60	0.268
70	0.422
80	0.235
100	0.622
140	20.582
200	40.600
270	25.950
Pan	11.990

The screen analysis of the natural base-material was made by sifting for 30 minutes 100 grams of the material obtained by quartering in the usual manner, using U.S.S. screens and a Rotap machine.

The base-material was tested for bond and permeability by the methods described and with the results given in Table 2. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9, and the permeability in Figure 10.

TABLE 2.—PROPERTIES OF THE NATURAL BASE-MATERIAL.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
4.11	385	1.274	88.9	37.3
6.03	465	1.538	107.5	37.3
7.97	515	1.704	119.0	37.5
9.97	539	1.782	124.5	36.4
12.28	564	1.865	130.25	35.2

The Natural Base-Sand.—The natural base-sand was prepared by removing the adsorbed material from the natural base-material. A large portion of the natural base-material was treated with 1 per cent caustic soda solution and shaken, then washed with water, and digested with hot 1-1 HCl to dissolve any film of hydrated oxides. The sand was washed repeatedly by decantation alternately at first with hot dilute acid and hot distilled water, finally with hot distilled water until the washings were free from acid. The sand after this treatment is hereafter referred to as the natural base-sand. This material was kept under distilled water which was changed frequently until no more acid, as determined by the colorimetric hydrogen-ion method diffused into the water. The base-sand was then collected and dried at 110° C. Its general appearance had changed from dull greenish brown to a light gray shot with sparkling bits of mica.

The iron oxide removed from the base-material by hot 1-1 HCl was determined and found to be 2.6 per cent. The total weight of ignited oxides removed by hot 1-1 HCl was 0.0272 grams per gram of sample or 2.72 per cent. This analysis indicated that practically all of the material removed by the HCl was iron of one form or another.

The natural base-sand was tested for bond and permeability by the methods described with the results given in Table 3. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

TABLE 3.—THE PROPERTIES OF THE NATURAL BASE-SAND.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.85	327	1.081	75.5	35.6
8.25	424	1.402	97.9	36.2
9.70	478	1.581	110.5	35.2
12.09	489	1.617	113.0	34.2

4. Synthesis of Molding Sand

In order to duplicate the properties of the natural base-material from the base-sand it is necessary to restore in all essentials the original surface conditions to the base sand. This was accomplished by adding to the base-sand a synthetic iron hydrosol in place of the natural colloid removed, thereby forming a synthetic base-material.

For the duplication of the properties of the natural molding sand from the natural or synthetic base-material it is necessary to restore the bond material in all essentials. This was accomplished by adding to the natural base-material and to the synthetic base-material, synthetic bond materials. In preparing the synthetic base-material and the synthetic molding sand, silica, kaolin and an iron hydrosol were used.

Preparation of Silica.—Two hundred pounds of pure fused silica ground to pass 100 mesh was procured from the Thermal Syndicate Ltd. of Brooklyn, N. Y. The principal impurity of this material was finely divided particles of iron, just enough so that when the silica was treated with dilute acid, a trace of iron was found by the sulphocyanate test.

A slight alkalinity was also noted in the first portions of wash water from the silica.

About 100 pounds of silica was washed by decantation with water from the still, until the washings showed no trace of their original alkalinity. Incidentally this treatment removed most of the finely divided iron and some dust. The silica was thrown onto a large Buchner funnel, where a large portion of the water was removed by suction. It was placed on a large block tin tray, air dried then dried at 110° C.

After drying the silica was thoroughly mixed and three samples of 2,000 grams each sealed in glass jars. The remainder of the silica was kept in a clean paper lined burlap sack from which it was drawn as needed. A portion of this sand was sifted through a 270-mesh sieve to provide fused silica for the synthetic "bond-material" No. 1.

Preparation of Kaolin.—A quantity of Merck's kaolin and also ten pounds of a non-plastic kaolin furnished by the research laboratory of the Norton Co. through the courtesy of Messrs. Kilpatrick and Beecher of that organization were washed by decantation with pure distilled water, dried at 105-110° C. and pulverized to pass 270 mesh.

Preparation of Iron Hydrosol.—The iron hydrosol or suspension of hydrated iron oxide was prepared by a method similar to that of Neidle and Barat.[28] Ninety grams of C.P. $FeCl_3.6H_2O$ was dissolved in 400 cc. H_2O. To this was added dropwise with constant stirring 150 cc. of ammonium hydroxide solution made by diluting 35 cc. 0.9 sp. gr. NH_4OH to 150 cc. The solution was allowed to stand for twenty-four hours, filtered through paper on a Buchner funnel, diluted to two liters,

[28] *J. Am. Chem. Soc.*, 39, 79 (1917).

and dialyzed cold in a collodion bag for twenty-four hours. The dialysis was continued at 70°-90° C. The collodion bags were changed each day for the first week and every other day thereafter until the dialysis was completed. This point was considered to be reached when 500 cc. of the solution from the interior of the collodion bags evaporated to 50 cc. showed no test for iron by the sulfocyanate method or chlorine by

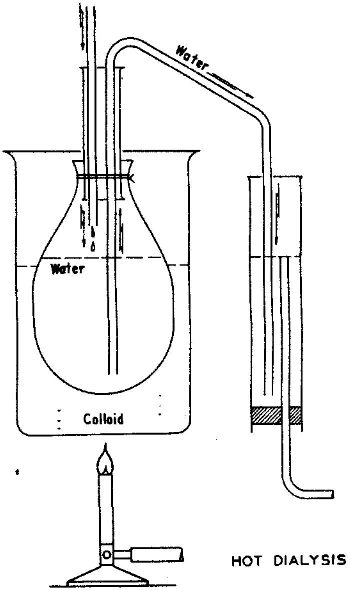


FIG. 11.

the usual procedure with silver nitrate. The analysis of the hydrosol, using the method of Thomas for chlorine and a gravimetric method for iron as iron oxide, gave the following result:

$$Fe_2O_3 : FeCl_3 = 15.01 : 1.$$

The general scheme of the dialyzing operation is shown in Figure 11. Two batteries of three dialyzing units in parallel (Figure 12) were each

fed from a five-gallon water bottle. The rate of feed during sixteen hours a day was about 1½ to 2 liters per hour, for the remaining eight hours approximately half of that rate. The outer containers were Vollrath enameled steel pans holding about six liters. Other than a slight stain on the enamal these pans showed no marked deterioration after one month's continuous use for this purpose. At the beginning of the operation ordinary distilled water was used. The dialysis was completed with pure water from the continuous still described above. The dialyzed

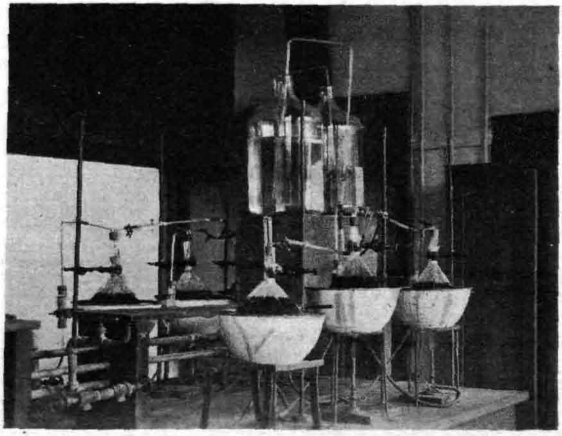


FIG. 12.

iron hydrosol was stored in glass bottles kept in a cupboard away from light.

Adsorption of the Iron Hydrosol.—The sand or clay particles were first wetted with water then mixed with the proper quantity of the iron hydrosol. The mixture of sand and hydrosol, or clay and hydrosol, was evaporated to dryness at or about 100° in a water bath, and in the case of the clay broken up so as to go through a 270 mesh sieve. For the sand sufficient hydrosol was used to give an Fe_2O_3 content of 1 per cent; for the clay the Fe_2O_3 was 0.44 per cent.

In preparing the synthetic bonds and sands the kaolin and sand, prepared separately as first described, were weighed out with an excess of water, mixed thoroughly and the excess water evaporated. The ma-

terial was air dried, then dried at 105° for one hour. This dry synthetic mixture was put through a sieve, one size larger than the largest grain of sand in the mixture, four times. The dry material was further mixed by spreading on a block tin platter and stirring systematically with a tin spoon, after which the synthetic molding sand was used directly in making up sand samples for testing.

Synthetic Bond Materials No. 1 and No. 2.—A chemical analysis of the clay-like bond material washed out of the molding sand was made. It will be noted that the water of composition of the kaolin is deducted from the total loss on ignition in the rationalized analysis.[29]

ANALYSIS OF NATURAL BOND MATERIAL

Chemical Analysis	Per cent	Rationalized Analysis	Per cent
Al_2O_3	6.20	Kaolin	15.4
Fe_2O_3	2.60	Fe_2O_3	2.6
SiO_2	86.10	SiO_2	78.86
Loss on ignition	3.6	Loss on ignition	1.6
CaO	.11	CaO	.11

From this analysis, assuming that all the alumina was in the form of kaolin and that both kaolin and silica grains were coated with hydrated iron oxide, a similar synthetic bonding material was made up of the proper amounts of fused silica and kaolin ground to pass 270 mesh and carrying adsorbed ferric hydrate. This material, referred to hereafter as synthetic bond No. 1 was air dried then dried at 105° for one hour and preserved in stoppered bottles until used.

Another bond material in which the fused silica passing 270 mesh was replaced by natural base-sand of the same size obtained from the original Albany molding sand was prepared. These grains were also coated with a film of hydrated iron oxide. The synthetic bond material so obtained will be referred to hereafter as synthetic bond No. 2. It was air dried, then dried at 105° for one hour, and preserved in stoppered bottles until used.

Base-Material No. 1.—The synthetic base-material No. 1 was made by adding to ground, fused silica of approximately the same screen analysis as the natural base material, in the manner described 1 per cent of hydrated iron oxide.

The synthetic base-material No. 2 was tested for bond and permeability by the methods described with the results given in Table 4. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9, and the permeability in Figure 10.

Synthetic Base-Material No. 2.—The synthetic base-material No. 2 was made by adding to the natural base-sand in the manner described 1 per cent of hydrated iron oxide.

[29] Mellor, *Trans. Eng. Ceram. Soc.*, **13** (1913-14); Samoylov, *Bulletin de l'Academie Imperial des Sciences de St. Petersburg*, **VI**, Ser. 31 (1909).

TABLE 4.—PROPERTIES OF SYNTHETIC BASE MATERIAL No. 1.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.97	684	2.16	158.0	22.2
6.09	787	2.60	183.5	24.2
7.93	822	2.72	191.5	24.6
10.04	838	2.77	195.0	25.0
11.93	885	2.92	206.0	25.7

The synthetic base-material No. 2 was tested for bond and permeability by the methods described and with the results given in Table 5. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9, and the permeability in Figure 10.

TABLE 5.—PROPERTIES OF NATURAL BASE-SAND PLUS 1 PER CENT HYDRATED IRON OXIDE, SYNTHETIC BASE-MATERIAL No. 2.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.85	385	1.274	88.9	33.4
8.2	540	1.786	125.6	34.2
10.31	560	1.852	129.4	32.0
11.93	570	1.885	131.7	31.5

Synthetic Molding Sands Nos. 1, 2, 3.—The synthesis of a molding sand having properties similar to those of the natural sand was accomplished in three independent ways. To natural base-material thirteen per cent of synthetic bond No. 1 was added. To the synthetic base material No. 2 thirteen per cent of synthetic bond material No. 1 was added. To the synthetic base-material No. 2 thirteen per cent of synthetic bond No. 2 was added.

The first synthetic molding sand No. 1, was tested for bond and permeability by the methods described and with the results given in Table 6. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

The second, synthetic molding sand No. 2, was tested for bond and permeability by the methods described and with the results given in Table 7. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

The third, synthetic molding sand No. 3, was tested for bond and permeability by the methods described and with the results given in Table 8. The compressive strength in grams per square centimeter is plotted as a function of moisture content in Figure 9 and the permeability in Figure 10.

TABLE 6.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 1.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.65	540	1.786	124.7	28.1
5.67	594	1.965	137.2	29.2
8.15	633	2.095	146.2	30.8
10.8	634	2.097	146.4	30.0
12.2	633	2.095	146.2	28.0

TABLE 7.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 2.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
4.06	578	1.912	126.1	28.2
8.11	646	2.138	150.0	29.2
10.33	656	2.190	152.5	28.6
12.17	642	2.123	149.0	28.2

TABLE 8.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 3.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.98	546	1.806	126.1	28.2
8.37	631	2.077	146.7	29.2
10.08	653	2.17	151.8	28.6
12.4	641	2.12	149.1	28.2

Discussion.—The graphs in Figure 9 show that the presence of the natural film of adsorbed material has a measurable effect on the strength of the base-sand. The absence of the bond material or "clay substance" causes a marked decrease in the strength of the natural molding sand. The graphs also indicate that the synthetic base-material No. 2 made from the natural base-sand and iron hydrosol is slightly stronger than the natural base-material; however, the agreement is good.

The general concurrence of the data on the strength of the synthetic molding sands as compared with that of the natural molding sands is good, and indicates that the physical strength of the natural molding sand has been substantially duplicated by that of the synthetic molding sands.

The graphs in Figure 10 show that the presence of the adsorbed film on the sand grains gives a slightly higher permeability than the sand alone. This fact and that the permeability of the natural molding sand rises to a maximum with increasing water content can be explained as due to swelling of colloidal particles and to the agglomeration of the sand grains with the bond material, thus causing larger envelopes of grain particles, with consequent lowering of resistance to air flow. When the pore space actually begins to decrease due to the filling up of the pore spaces with water the permeability to gases decreases.

The agreement of the values of permeability of the different synthetic sands is satisfactory. The permeability of the synthetic sands is more nearly constant with varying water content, which in foundry work is to be desired.

An interesting sidelight is had on the influence of grain shape by observing the behavior of base-material No. 1 made up of ground fused silica of the same screen analysis as the natural base-material. In this instance the only variable is the shape of the grain. The angular grains of the crushed silica have a higher strength and lower permeability than the more rounded grains of the natural base-sand which has a lower strength and higher permeability. This function of grain shape and permeability was first recognized and accounted for by King and Schlichter.[30] Angular grains when packed together have, in general, more pore space and are less permeable.

5. The Effect of Heat on Natural and Synthetic Molding Sands

The behavior of molding sands when heated has been studied by a number of investigators. The experience of Dietert [31] and Littlefield [2] indicates that the loss of bond observed on heating a natural molding sand to 600° F. for two hours gives a good indication of its utility as a molding sand. It is interesting to note in this connection that von Weiman and Hagiwara [32] have shown that Goethite, natural crystalline ferric hydrate ($Fe_2O_3 . H_2O$), loses most of its water when treated at 608° F. (320° C.). However hydrated iron oxide [33] appears to be the only metallic hydroxide that will adsorb water and regain its initial surface condition after being dried or heated to 315° C. (600° F.) or above.

For the purpose of indicating the relative durability of the synthetic and natural molding sands, the samples were heated at 600° F. for three hours, then moistened and tested in the manner described. This treatment is more severe than that recommended by Dietert [34] and Littlefield [2] in that heating was continued for three hours instead of two.

The heating of the sand was done in an ordinary Freas thermostatic oven provided with a large capacity heating coil and a heavy-duty thermo-regulator. The temperature was recorded on a calibrated Tycos nitrogen filled mercury thermometer the bulb of which was thrust into the sand being heated, care being taken that the thermometer bulb did not touch the metal pan. As the thickness of the sand layer in the pan

[30] *U. S. Geol. Survey*, 19th Annual Report (1899).
[31] *Trans. Am. Foundrymen's Assoc.*, 32, 24-52 (1924).
[32] "Colloid Chemistry," edited by Jerome Alexander, Vol. I, p. 653. Chem. Cat. Co., New York, 1926.
[33] Paneth and Vorwerk, *Z. physik. Chem.*, 101, 445 (1922); Hahn and Muller, *Z. Elektrochem.*, 29, 189 (1923); Hahn, *Naturwissenschaften*, 12, 1140 (1924); *Liebigs Ann.*, 440, 121 (1924).
[34] *Trans. Am. Foundrymen's Assoc.*, 32, 24-52 (1924).

did not exceed one-half inch a small part of the thermometer bulb was exposed to the heated air of the thermostat. The temperature of the thermostat was held constant to ± 2° F.

The dry samples of sand were spread in layers one-half inch thick in a black iron baking pan, placed in the oven, and allowed to come to a temperature of 600° F. at which temperature the material was held for three hours.

Properties of Natural Molding Sand, Heated.—The natural Albany molding sand heated at 600° F. for three hours was tested for bond and permeability by the methods described with the results given in Table 9. The compressive strength plotted as a function of the moisture content is shown in Figure 9 with that of the untreated sand for comparison. The permeability plotted as a function of moisture content is shown in Figure 10.

TABLE 9.—PROPERTIES OF NATURAL ALBANY MOLDING SAND HEATED TO 600° F. FOR THREE HOURS.

Percentage H_2O	Breaking Strength in Compression: 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.6	467	1.545	108.6	35.9
6.46	547	1.760	127.2	37.8
8.11	597	1.975	138.8	33.1
9.82	609	2.013	141.6	32.4
12.32	602	1.99	140.0	30.1

Properties of Synthetic Molding Sands Nos. 1, 2, and 3.—Synthetic molding sands Nos. 1, 2, and 3 heated to 600° F. for three hours were tested for bond and permeability by the methods described

TABLE 10.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 1 (NATURAL BASE MATERIAL PLUS SYNTHETIC BOND No. 1, HEATED).

Percentage H_2O	Breaking Strength in Compression: 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.92	476	1.57	110.8	33.2
5.95	558	1.84	129.8	33.0
8.2	610	2.01	141.9	34.1
9.9	613	2.02	142.6	31.3
12.1	630	2.08	146.5	30.6

TABLE 11.—PROPERTIES OF SYNTHETIC MOLDING SAND No. 2 (SYNTHETIC BASE MATERIAL No. 2 PLUS SYNTHETIC BOND MATERIAL No. 1), HEATED.

Percentage H_2O	Breaking Strength in Compression: 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.95	491	1.62	114.2	32.4
7.40	614	2.03	142.8	32.9
9.65	621	2.068	144.3	29.8
12.16	629	2.08	146.3	29.6

with the results given in Tables 10, 11 and 12. The compr strengths are plotted as a function of the moisture content in Fig and the permeabilities in Figure 10.

TABLE 12.—PROPERTIES OF SYNTHETIC MOLDING SAND NO. 3 (SYNTHETIC MATERIAL NO. 2 PLUS SYNTHETIC BOND MATERIAL NO. 2), HEATED

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Perme
4.02	458	1.51	106.4	34
8.16	608	2.01	141.4	34
10.31	602	1.99	140.0	30
12.63	598	1.97	139.0	28

Discussion.—The strength of the natural and synthetic m sands are decreased to almost the same degree by heating to 60 for three hours. This affords further evidence that the natural m sand has been substantially duplicated by synthetic means.

The permeabilities of the natural and synthetic sands are inc to about the same degree by the heat treatment.

The data presented indicate that the bond, permeability, and bility of high grade natural molding sand can be substantially dupl by synthetic means using adsorbed ferric hydrogel as a bonding a

6. BONDED SYSTEMS FROM PURE INGREDIENTS

The numerous constituents of natural molding sand identifi Condit [35] are not essential to the properties of molding sand. I just been shown that the properties of a high grade molding sanc be duplicated by the use of only three materials, sand, kaolir ferric hydrosol. For scientific reasons, at least, it is desirable bonded systems of pure silica, kaolin and ferric hydrosol be invest as well as the ordinary molding sand. The material used for this pose were the ground fused silica, the kaolin and the ferric hydros ready described.

The Bond Material.—The bond material used in the case c pure materials was kaolin and kaolin treated with 0.44 per cent oxide as hydrated iron oxide. The kaolin untreated with the hy was used to determine the effect of the absence of hydrated iron Fifteen per cent by weight of kaolin or kaolin plus 0.44 per cen oxide was used as the bond material in this work with pure mat

Base Silica.—In the synthesis of the molding sand previousl scribed the base sand furnished the starting point. In this cas ground fused silica was used.

The base silica was tested for bond and permeability by the me described and with the results given in Table 13. The compr

[35] *Trans. Am. Foundrymen's Assoc.*, 21, 19-52 (1912).

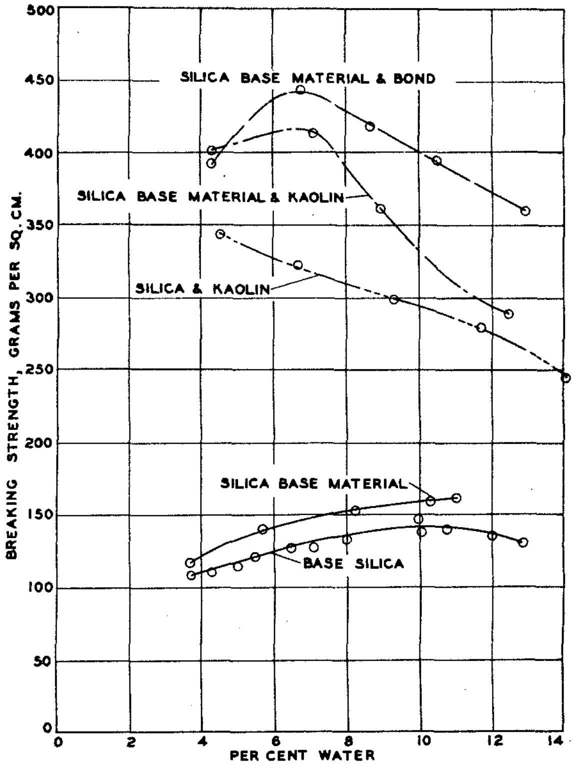


FIG. 13.

strength as a function of moisture content for the three samples is plotted in Figure 13 and the permeability in Figure 14.

Silica Base Material.—The synthesis of the silica base material was accomplished by the same method used in the preparation of the base material of the synthetic molding sand, using the base silica and

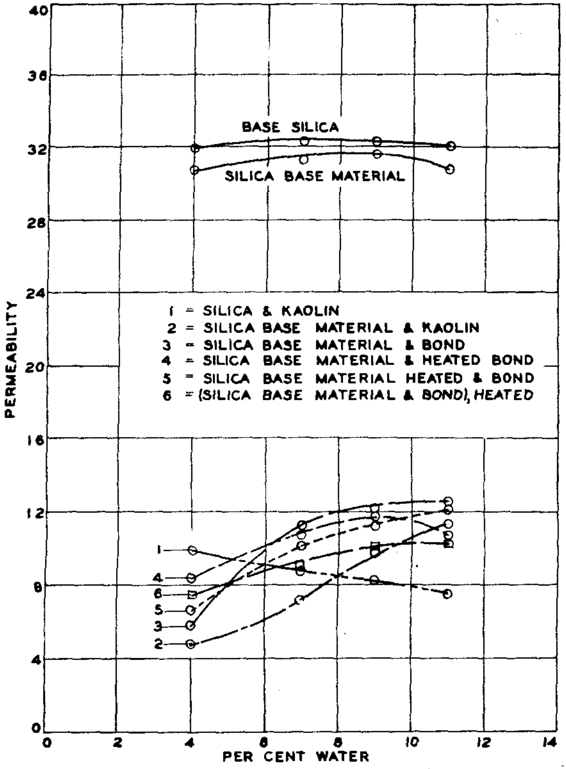


FIG. 14.

ferric hydrosol. One per cent of ferric oxide as hydrosol was added to the silica.

The silica base-material was tested for bond and permeability by the methods described. The results are plotted in Figures 13 and 20 as well as Table 14.

TABLE 13.—PROPERTIES OF BASE SILICA.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
3.69	466	1.541	108.6	..	...
4.32	480	1.587	110.9	4	32.0
5.01	497	1.644	115.6	..	...
5.5	524	1.733	121.1	..	...
6.48	546	1.806	126.2	7	32.4
7.17	547	1.81	127.2	..	...
8.0	575	1.902	132.9	..	...
10.06	634	2.098	146.5	..	...
10.1	597	1.975	138.0	9	32.4
10.82	602	1.991	140.0	..	...
12.0	594	1.965	135.9	..	...
12.9	570	1.885	131.7	11	32.1

TABLE 14.—PROPERTIES OF SILICA BASE-MATERIAL (BASE SILICA PLUS 1 PER CENT HYDRATED IRON OXIDE).

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
3.66	498	1.647	115.7	4	30.8
5.74	602	1.99	140.0	7	31.4
8.32	656	2.17	152.5	9	31.7
10.35	686	2.27	159.5	11	30.8
11.05	690	2.28	161.0	..	...

Mixture of Silica and Kaolin.—A mixture of 85 per cent ground fused silica and 15 per cent kaolin was prepared in the manner described.

The mixture of silica and kaolin was tested for bond and permeability by the methods described with the results given in Table 15 and plotted in Figures 13 and 14.

TABLE 15.—PROPERTIES OF SILICA-KAOLIN MIXTURE.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
4.53	1482	4.90	344.3	4	9.9
6.66	1337	4.42	322.0	7	8.8
9.33	1288	4.26	299.3	9	8.4
11.76	1207	3.99	280.8	11	7.6
14.14	1064	3.518	245.0	..	...

Silica Base Material plus 15 Per cent Kaolin.—The combination of the silica base-material and 15 per cent kaolin was brought about in the same manner and tested with the results given in Table 16 and plotted in Figures 13 and 14.

TABLE 16.—PROPERTIES OF SILICA BASE MATERIAL PLUS 15 PER CENT KAOLIN.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
4.28	1728	5.71	401.5	4	4.8
7.05	1783	5.895	414.5	7	7.2
8.96	1555	5.14	361.5	9	9.9
12.46	1243	4.11	289.0	11	11.4

Silica Base Material plus 15 Per cent "Bond Material" (Kaolin with 0.44 Per cent Iron Oxide as Hydrated Iron Oxide).—To the silica base-material 15 per cent of kaolin containing 0.44 per cent of iron oxide was added in the manner described.

The combination of silica base material with kaolin carrying 0.44 per cent iron oxide as hydrated iron oxide was tested for bond and permeability by the methods described and with the results given in Table 17 and plotted in Figures 13 and 14.

TABLE 17.—PROPERTIES OF SILICA BASE MATERIAL PLUS 15 PER CENT KAOLIN CONTAINING 0.44 PER CENT IRON OXIDE AS HYDRATED IRON OXIDE.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
4.23	1688	5.58	392.2	4	5.8
6.72	1911	6.32	444.0	7	11.3
8.65	1804	5.96	418.2	9	12.3
10.50	1700	5.62	395.0	11	12.6
12.93	1548	5.115	360.0	..	...

Discussion.—The presence of the surface film of hydrated iron oxide on the fused silica base causes an increase in the strength of the material similar in character to that observed when the natural base-sand was treated with the iron hydrosol.

The presence of the hydrated iron oxide film on the silica is shown to exert a marked influence on the strength of silica-kaolin mixtures. Hydrated iron oxide films on both silica and kaolin give a further increase in strength, especially at the higher water contents.

The permeability of the silica-kaolin mixtures decreases with successive additions of water while the permeability of the silica-kaolin-iron oxide combinations shows an increase with water content. This may be taken as an indication that adsorbed hydrated iron oxide on the particles of silica is present as a gel which takes up water and swells thereby forming larger particles tending to become spherical or causing the separate grains to agglomerate, in either case increasing the permeability of the mass.

7. The Cause of the Decrease in Bond on Heating

The effect of heating the silica-kaolin-iron hydrogel system was investigated to determine the probable cause of the decrease in bond on heating. For this purpose the silica base material and the bond material were heated separately, then mixed with unheated bond and base material respectively, and compared with the mixture of unheated material and the bonded system mixed before heating.

The kaolin bond material containing the adsorbed hydrated iron oxide was heated at 600° F. for three hours, cooled to room tempera-

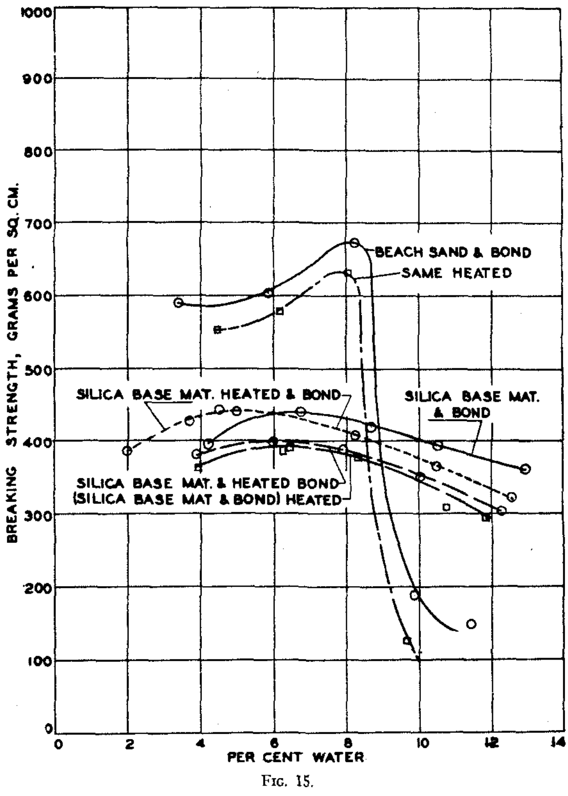


Fig. 15.

ture, and mixed with the silica base material in the manner described. This mixture was tested for bond and permeability with the results given in Table 18 and plotted in Figures 14 and 15.

The silica base material was heated at 600° F. for three hours, cooled to room temperature, and combined with the kaolin bond mate-

TABLE 18.—PROPERTIES OF THE SILICA BASE-MATERIAL PLUS (KAOLIN CONTAINING 0.44 PER CENT IRON OXIDE AS HYDRATED IRON OXIDE, HEATED TO 600° F. FOR THREE HOURS).

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
3.9	1650	5.455	383.5	4	8.4
6.0	1720	5.685	400.0	7	10.8
7.95	1680	5.528	390.5	9	11.85
10.1	1515	5.02	352.0	11	10.8
12.3	1307	4.32	304.0	..	...

rial in the manner described. This mixture was tested for bond and permeability with the results given in Table 19 and plotted in Figures 14 and 15.

TABLE 19.—PROPERTIES OF SILICA BASE MATERIAL HEATED AT 600° F. FOR THREE HOURS PLUS 15 PER CENT KAOLIN CONTAINING 0.44 PER CENT IRON OXIDE AS HYDRATED IRON OXIDE.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
2.0	1673	5.515	389.0	4	6.7
3.7	1850	6.116	430.0	7	10.2
4.55	1918	6.34	446.0	9	11.3
5.0	1898	6.274	441.0	11	12.1
8.25	1741	5.76	409.5	..	...
10.55	1576	5.21	366.2	..	...
12.6	1393	4.60	322.9	..	...

The silica base-material was mixed with the bond material (kaolin with 0.44% iron oxide as hydrated iron oxide) and the mixture heated at 600° F. for three hours. This heated mixture was tested for bond and permeability with the results given in Table 20 and plotted in Figures 14 and 15.

TABLE 20.—PROPERTIES OF SILICA BASE MATERIAL PLUS 15 PER CENT KAOLIN CONTAINING 0.44 PER CENT HYDRATED IRON OXIDE, HEATED AT 600° F. FOR THREE HOURS AFTER MIXING.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Percentage H_2O	Permeability
3.96	1575	5.204	366.0	..	...
6.28	1670	5.51	388.0	4	7.5
6.42	1695	5.60	394.0	7	9.1
8.4	1635	5.40	380.0	9	10.0
10.8	1333	4.405	310.0	11	10.4
11.86	1296	4.222	295.0	..	...

Discussion.—Heating the silica base before mixing it with the bond material has no noticeable effect on the maximum strength of the bonded system. This indicates that the loss in bond on heating, at least to 600°

F. for 3 hours, is not due to any change in the ferric hydrogel adsorbed on the silica. This fact is a further verification of that reported by Hahn [33] that hydrated ferric oxide is reversibly peptized on heating. Heating the silica base does seem to shift the point of maximum bond toward drier mixtures from about 7 to 5 per cent water content. This may be due to the heated gel being more easily wetted and therefore weaker at the higher water contents.

On the other hand, heating the bond material before mixing with on the silica. This fact is a further verification of that reported by lost on heating. This clearly indicates that the loss in bond on heating is due entirely to changes in clay bond. Although the mineral kaolinite ($Al_2O_3.2SiO_2.2H_2O$) has shown no evidences of decomposition at temperatures as low as 600° F. [36] other hydrous aluminum silicates probably present in kaolin such as Halloysite and Allophane [37] show evidences of dehydration at temperatures as low as 300° F. (150° C.). Bigot reports that clays are partially irreversibly pektized at 350° to 600°.

With these facts in mind it seems evident that the loss in strength on heating is due to changes in the clay, either by decomposition of the crystal structure or by changes in surface conditions, and not due to changes in the sand particles or in the ferric hydrogel.

High Grade Molding Sand from Unbonded Beach Sand

The results of this work clearly indicate the possibility of preparing high grade synthetic molding sands to meet specifications for certain uses. As a demonstration a clean beach sand from the Michigan City district was mixed; treated with iron hydrosol and mixed with 15 per cent kaolin containing 0.44 per cent hydrated iron oxide as described. This synthetic material was tested for bond and permeability by the methods described with the results given in Table 21 and plotted in Figure 15.

Table 21.—Properties of Michigan City Sand Base Material Plus 15 Per cent Kaolin Containing 0.44 Per cent Hydrated Iron Oxide.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
3.41	2525	8.44	592.0	...
5.90	2600	8.6	604.0	...
8.32	2910	9.63	676.0	45
9.89	813	2.69	189.0	...
11.44	641	2.12	149.0	...

[36] S. Satoh, *J. Am. Cer. Soc.*, **4**, 182 (1921).
[37] Le Chatelier, *Compt. rend.*, 104, 1443 (1887); Ding. polyt. J., 265, 94 (1887); A. Bigot, *Compt. rend.*, **178**, 91 (1923).

The same sample was dried and heated at 600° F. for three hours, then tested for bond and permeability, with the results given in Table 22 and plotted in Figure 15.

TABLE 22.—PROPERTIES OF MICHIGAN CITY BASE MATERIAL PLUS 15 PERCENT KAOLIN CONTAINING 0.44 PER CENT HYDRATED IRON OXIDE HEATED TO 600° F. FOR THREE HOURS.

Percentage H_2O	Breaking Strength in Compression 2/3 Gms. per Sq. In.	Lbs. per Sq. In.	Gms. per Sq. Cm.	Permeability
4.5	2390	7.92	556.0	...
6.2	2500	8.38	581.0	...
8.1	2720	9.02	633.0	55
9.7	540	1.79	125.5	...
12.0	wet	...	....	...

University of Michigan,
Ann Arbor, Michigan.

HYDRATED PORTLAND CEMENT AS A COLLOID

By Alfred H. White

Portland cement clinker is composed in part of rather definite crystalline compounds and in part of amorphous slag. There is some dispute about the exact formula for the definite compounds, but it is agreed that they are basic silicates and aluminates of lime. When water is brought in contact with ground clinker, the constituents react and form compounds which are in part crystalline and in part amorphous. The character of these hydrated compounds depends upon a number of factors, but largely upon the amount of water used. Several investigators have attempted to determine the products formed when cement reacts with an excess of water, but have only established that the products hydrolyze, as was to have been expected, calcium hydroxide going into solution and more siliceous products remaining in the solid state. Treatment of these solid products with successive portions of fresh water gave a continually changing product without a definite limit being reached. This procedure throws very little light upon the reactions when Portland cement is used as a structural material, for an excess of water is never employed when Portland cement is used in practice, and the calcium hydroxide formed through decomposition of the cement clinker separates in the solid phase as one of the constituents of the concrete. In practice, from 50 to 75 pounds of water are used for each 100 pounds of cement.

There is no definite or theoretical amount of water which can be said to enter into combination with Portland cement. For gypsum, which is one of the simplest hydraulic cements, a definite equation is usually written with the final product expressed as $CaSO_4.2H_2O$. Portland cement has various components and some of them, at least, do not form crystalline compounds. The case is further complicated by the fact that even though the cement is very finely ground, it is only the external surface of the fine cement particles which react with water. If concrete which has been under water for years is examined microscopically, it will be found that there are still nuclei of unchanged Portland cement clinker which have failed to hydrate.

The first clear treatment of the reactions which take place on the hydration of Portland cement was contained in a study by H. Le

Chatelier [1] in 1889. The next important contribution was made in 1893 by Michaelis,[2] who enunciated the colloidal theory of the hydration of cement.

It was H. Le Chatelier [3] again who in 1900 showed that there was an absolute decrease in volume of the wet paste during the hardening process. This was later confirmed by Kühl,[4] one of whose experiments may be cited. A paste made from 250 grams of cement and 200 cc. of water was put into a graduated flask and the space remaining above the paste was filled to the graduated mark with clear water. There was a shrinkage after three hours of 1.4 cc., after twenty-four hours of 5.0 cc., after seven days of 10.6 cc., and after twenty-eight days of 13.6 cc. All cements showed this contraction which continued up to the time when expansion of the cement in the bulb of the flask cracked the glass.

Quantitative measurements of the slow expansion of cement while it lay in water were first made by Bauschinger [5] in 1879. It became well established that bars of wet Portland cement expanded during the first year of immersion in water and then reached a steady state with an elongation of from 0.10 to 0.15 per cent. It was also well known that bars of wet cement kept continuously in air after they were removed from their molds, showed a shrinkage for several months, but ultimately reached a fairly steady state with a decrease in length of from 0.24 to 0.39 per cent.

Expansion and Contraction with Change in Moisture Content.—It fell to the present author [6] to first show that cement bars which had reached a steady state in either air or water, changed their length with their moisture content and could be made to vary from 0.15 to 0.25 per cent in length with each alteration between the wet and the dry state.

This is illustrated in Figure 1 which shows the changes which have taken place in two bars of neat cement during a period of more than 19 years. Both *E* and *G* were commercial cements complying with standard specifications which were made into bars approximately 100 mm. long and 25 mm. square with glass plates cast in the ends to give a smooth surface of contact for the micrometer. They were mixed with water to normal consistency, molded and kept damp for 24 hours, after which they were removed from the molds and measured. This measurement was taken as the zero measurement and all elongations were recorded as plus variations, and all contractions as minus varia-

[1] *Annales des Mines*, 1887, p. 345.
[2] *Chem. Ztg.*, 17 (2), 1243 (1893).
[3] *Bul. Soc. de l'Encouragement*, 5th Series V, 5, p. 54.
[4] *Tonind. Ztg.*, 36, 1331 (1912).
[5] *Mitt. Lab. Techn. Hochschule Munchen*, Heft 8, 1879.
[6] *Proc. Am. Soc. Test. Mat.*, 11, 531 (1911); 14, 203 (1914).

tions from this original zero length. It will be noted that in each case there was slow expansion while lying in water at room temperature and that a constant length was reached after a year. After approximately three years in water the bars were placed in dry air at room temperature with a resultant gradual contraction which caused the bar to become shorter than its initial measurement. On reimmersion in water expansion resulted and this same cycle of changing length has been repeated with each change in environment.

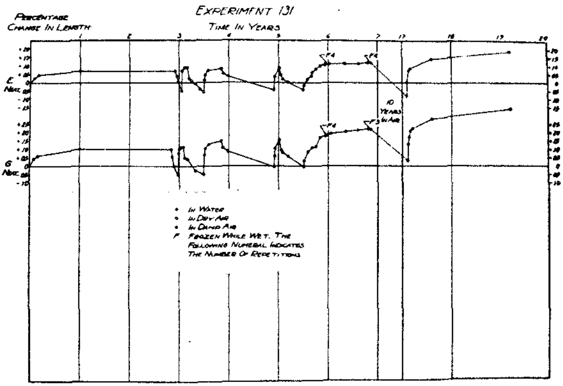


FIG. 1.—Percentage changes in length of bars of neat cement when wet, dried, exposed to damp air and frozen while wet.

This behavior is not peculiar to these two cements, but is characteristic of all Portland cements, even those of rather unusual composition. The obvious explanation is that the colloidal gel maintains its reversibility at atmospheric temperature for a very long time. The behavior of bars made in this laboratory which have been under observation for more than 20 years substantiate this explanation and test bars cut from old sidewalks permit the conclusion to be extended to still older specimens.

The alternations in length as shown in Figure 1 not only continue without diminution but actually increase in amplitude with successive swings. This is quite clearly due to the incomplete hydration of the particles of Portland cement clinker. Microscopic examination of bars of cement which have been in water many years shows unchanged

nuclei of cement clinker imbedded in a dense mass of alteration products. Water continues to act on the clinker until the gel becomes packed so tightly that no more water can force its way through. The cement or concrete will retain this condition unchanged so long as it is immersed in water. If the water is removed by evaporation, the dehydrated gel shrinks and the mass becomes porous. When it is again

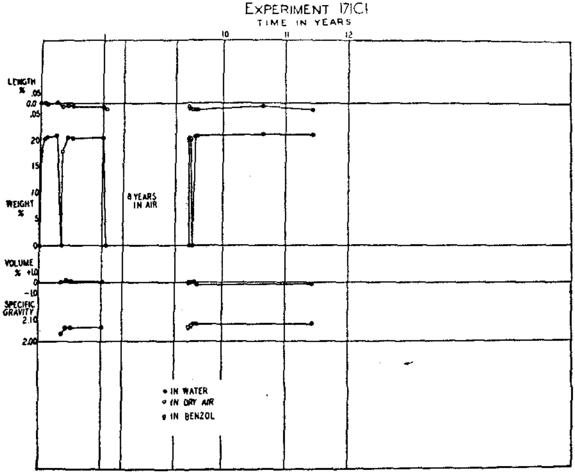


FIG. 2.—Percentage changes in length, weight and volume, and variations in apparent specific gravity of a clay brick when wet, dried and immersed in benzene. The values for increase in weight and specific gravity on immersion in benzene have been recalculated to the basis of water.

immersed in water, capillary action carries the water rapidly through the shrunken colloid to the particles of unchanged clinker with the result that additional hydration products are formed with a consequent increase in length over anything attained previously. On the first reimmersion in water at the end of the third year the expansion was about 0.15 per cent. The latest immersion for two years shows an expansion of 0.27 per cent for one cement and 0.31 per cent for the other.

The effect of damp air is also shown in Figure 1 where, between the fifth and sixth years, the bars after being air-dried were exposed to air almost completely saturated with water at room temperature. It will be noted that almost two-thirds as much expansion took place in damp air as on previous immersion in water for a similar period. The expansion of Bar *E* in damp air amounted to 0.08 per cent in two months, and the expansion of Bar *G* amounted to 0.12 per cent after three months in damp air.

The effect of freezing is indicated on these same curves by the letter *F* which indicates that the bar was frozen while saturated with water. It will be seen that several successive freezings did not affect the length of the bar materially. A fuller study will be found further on in this paper.

Behavior of a Clay Brick.—The behavior of a clay brick when immersed in water is shown in Figure 2. This was a common brick taken from an old stuccoed building which was being torn down. An expansion bar was sawed from it, and studies were made, not only of changes of length but also of changes in weight and apparent specific gravity. The changes in length between the wet and dry state are less than one-tenth those noted with neat Portland cement and amount to only about 0.02 per cent. The brick is rather soft burned and porous and absorbs 90 per cent of the total water in two hours, and practically all of its water within a few days. The apparent specific gravity rises in the same period from 2.03 to 2.08 and stays constant. As a check on some later work, figures were obtained on immersion in benzol with a similar result. To make the figures comparable on the graph, the changes in weight and specific gravity on immersion in benzol are calculated to what they would have been if benzol had the same density as water.

Changes in Volume, Weight and Specific Gravity of a Cement Bar in Benzene and in Water.—A more detailed study of the effect of water on a bar of neat cement is given in Figure 3. This was a commercial cement which passed the standard specification and was made into a paste of normal consistency and molded into a bar. The bar was removed from the mold after 24 hours and measured. It was then kept alternately in air and water as shown on the graph and gradually became longer so that its length at the end of five years was +.23 per cent when it had been soaked in water for about a year. It was then set aside and allowed to rest for eight years in air dried with calcium chloride. When experiments were resumed, the bar was first soaked in benzene, then dried, and again immersed in water.

Details of the behavior of the bar in benzene and in water are given in the lower part of Figure 3, although even in the detail the scale is not large enough to permit all of the tests to be shown.

The dried bar was first immersed in benzene in a vessel which was evacuated until the benzene boiled, and the bar was kept immersed in the benzene boiling at room temperature for half an hour. The bar was then measured, weighed in air, and suspended in benzene so that its specific gravity could be calculated. It was at once put back in benzene which was boiled at room temperature for another half hour. This

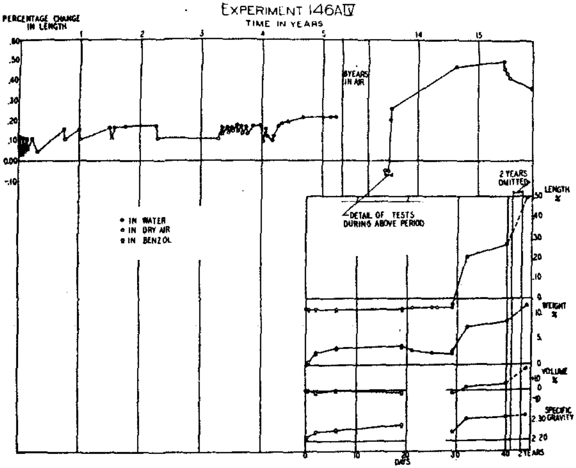


FIG. 3.—Percentage changes in length, weight, and volume, and variations in specific gravity of a bar of neat cement when wet, dried, and immersed in benzene. The values for increase in weight and specific gravity on immersion in benzene have been recalculated to the basis of water.

was repeated five times and yet after these treatments, the bar had absorbed less than 0.4 per cent of benzene by weight. It was then allowed to lie in benzene at atmospheric pressure with occasional measurements, as shown on the graph, for 19 days. It increased in weight 3.5 per cent in this period and its apparent specific gravity rose from 2.218 to 2.279, but its length and its volume as determined by the benzene displaced did not change in any significant manner.

The slow infiltration of the benzene indicates that the capillaries were very small. Other work in this laboratory has shown that the

capillaries of old cement bars become almost choked at the surface with calcium carbonate formed from calcium hydroxide which is drawn to the surface through the evaporation of water. The capillaries of the interior of the bar were probably not so minute as those at the surface. It seems fairly evident that the only action taking place in benzene was the slow infiltration of the liquid which gradually filled the capillaries, causing an increase in weight and apparent specific gravity without any measurable increase in length or volume. In the graph of Figure 3, the increases in weight and volume have been recalculated to what would have been shown if benzene had the same density as water. This allows a direct comparison on the graph. The bar was then removed from the benzene and placed in a stream of dry air for 10 days. This was not long enough to remove all of the benzene since the weight did not drop entirely to the initial figure.

The next step was to immerse the bar in water and an attempt was made as with benzene to accelerate the infiltration by a partial vacuum. The increase in weight during the first half hour's immersion was only 0.13 per cent, but on subsequent immersions at atmospheric pressure, water continued to be absorbed, slowly to be sure, but distinctly more rapidly than was the case with benzene. A more noteworthy difference was the expansion that accompanied the absorption of water. In three days the linear expansion amounted to 0.23 per cent and it rose more gradually as shown by the graph to a total linear change of 0.52 per cent in two years. The changes in volume computed from the weight of water displaced are even greater than those obtained by direct linear measurement and indicate that the water had not penetrated to the center of the bar, only 25 mm. square, even after two years. It is probable that the colloid in the outer envelope became so dense that no more water could force its way through it. The bar was, therefore, not homogeneous but consisted of an expanded envelope in compression surrounding a core which was in tension. The measurements of length reflected the resultant of these two opposing stresses.

The graph of Figure 3 ends with a record of the length of the bar after six months in dry air. At the present time the bar has been in dry air for two years and one month, but it is still showing a length of +0.315 per cent and a weight of only +0.95 per cent. There is a permanent expansion out of all proportion to the amount of water retained. This is explicable on the theory of hydration of clinker which had not been in contact with water previously.

Internal Pressures Produced by Adsorption of Water.—An excellent review of the heat effects produced by adsorption and the consequent pressures which may be calculated has been given by Browne

and Mathews.[7] Lamb and Coolidge[8] showed that the compression of vapors adsorbed by charcoal as indicated by the heat of adsorption was in the neighborhood of 37,000 atmospheres. Harkins and Ewing[9] determined the volume of liquid adsorbed by thoroughly outgassed charcoal and calculated that water in the micropores of charcoal may be compressed about 25 per cent. Nutting[10] has recently calculated that the compression of water on the surface of silica sand may be 17,000 atmospheres.

It is not feasible to apply the technique of these investigators to Portland cement because heat is evolved in the chemical reactions accompanying the hydration of cement. The hydration does not become complete but fresh chemical action takes place with every immersion in water so that it is not possible to obtain reliable figures from the heat effects. Neither is it possible to pump out adsorbed gases completely because hydrated cement is altered by heat and gives up moisture for a long time in even a very incomplete vacuum. No attempt has, therefore, been made to determine the heat effects due to adsorption.

An attempt has been made to draw some conclusions from the increase in specific gravity. The apparent specific gravity of these bars was determined by weighing the bars while suspended in water (or benzene), removing from the liquid, wiping off the surface liquid, and weighing the bar quickly in the air. This latter process involved an error of appreciable magnitude which was reflected in an error of about three points in the third decimal place in the specific gravity. This was not large enough to obscure the trend of the results which change in the case of the bar of Figure 3 from a specific gravity of 2.218 to one of 2.324 which is 35 times the probable error. The meaning of the increase in specific gravity is obscured by the compression of the gas remaining in the voids.

The slope of the curve of Figure 3, showing increase in weight when immersed in benzene, indicates that absorption was nearly complete in 19 days. The absorption of benzene did not cause any measurable increase in volume but did cause an increase of apparent specific gravity due to slow displacement or compression of the air in the capillaries. The absorption of water caused an increase of ten per cent in volume and an increase in specific gravity much larger than that caused by benzene.

If it could be assumed that the volume of water in the capillaries was equal to the volume of benzene previously absorbed, and that the balance of the water was adsorbed in the micropores and was responsible for the expansion noted, it would permit calculation of the compression

[7] Alexander, "Colloid Chemistry," Vol. 1, pp. 450-470. Chemical Catalog Co., 1923.
[8] *J. Am. Chem. Soc.*, **42**, 1146 (1920).
[9] *J. Am. Chem. Soc.*, **43**, 1767 (1921).
[10] *J. Phys. Chem.*, **31**, 531 (1927).

of the water. On this basis it would appear that the water in the micropores was compressed to less than half its initial volume. The uncertainties surrounding this calculation are evidently large, and little reliance is attached to it, except as a qualitative indication that pressures of large magnitude are involved.

Other evidence of the pressures developed may be found in the expansion in damp air noted in Figure 1. The data are more complete for Bar *G* and the numerical data for the test on this bar are given in Table 1.

It is apparent that the increase in length proceeds more rapidly than the increase in weight. It is probable that it is the expansion of the outer layer which affects the length and that the slower penetration of moisture to the center relieves the tensile strains but does not cause commensurate increase in volume. Immersion in water causes further expansion and increase in weight as shown.

TABLE 1.—CHANGES IN LENGTH AND WEIGHT OF A BAR OF NEAT CEMENT IN AIR SATURATED WITH MOISTURE AT ROOM TEMPERATURE.

	Change in Length Per Cent	Change in Weight Grams
On removal from dry air	—.002	138.95
7 days in damp air	+.028	
1 month in damp air	+.085	
2 " " " "	+.103	141.37
3 " " " "	+.116	142.35
2 hours in water in vacuum	+.125	144.00
1 month in water	+.174	146.67
2 " " "	+.178	146.80

External Pressures Produced by Adsorption of Water.—The high pressures which have been determined by others as existing in the micropores of loose granules do not indicate the pressures which might be directed externally to cause deformation of solid bodies. The expansion of concrete gives some measure of this external pressure although the situation is complicated by the probability that some fresh cement clinker is hydrated every time that concrete is moistened.

Hydrated cement is, to some extent, plastic and has no well-defined modulus of electricity. A figure of 5,000,000 pounds per square inch is, however, rather frequently taken as an approximation of the modulus for rich mortars which have had adequate opportunity to harden. On this assumption, an elongation of 0.1 per cent corresponds to a stress of 5000 pounds per square inch. This is about the load which rich concrete will bear in compression, and from five to ten times the amount it will bear in tension.

The effect of expansion is evidenced in pavements and other structures exposed to the weather. The magnitude of the stress is in many

cases sufficient to cause pressure ridges or upheavals in the concrete. The stresses produced by changes in moisture content constitute the fundamental cause of the disintegration of concrete as has been set forth more fully by the author elsewhere.[11]

Effect of Freezing While Saturated with Water.—Freezing cement bars while they are saturated with water should cause an expansion which is a function of the amount of liquid water which the bars contain. Experiments were made by measuring the bars when removed from water, freezing them, measuring them while frozen, thawing them under water and measuring them again. The chief error in this work is due to the change in the length of the cast iron yoke of the micrometer with change in temperature. The coefficient of expansion of cast iron is closely that of cement, and the variation has not been determined for the lower temperatures. In this work, it has been assumed that the correspondence remains the same, and only the differential change in length between cast iron and cement has been measured. That this experimental procedure is adequate is shown by the following illustration: A bar of rich lime mortar containing some Portland cement had hardened for several months. It consisted of grains of sand, bonded together with crystalline calcium carbonate and a small amount of Portland cement. Its water absorption was 15.1 per cent. This bar, frozen while saturated with water and measured while frozen at 27° F., showed an elongation due to freezing of 0.085 per cent.

The neat cement bars of Figure 1 showed on the contrary an apparent contraction when frozen, the contraction becoming greater at the lower temperatures. Some data are given in Table 2.

TABLE 2.—VARIATIONS IN LENGTH OF A BAR OF NEAT CEMENT SUCCESSIVELY FROZEN AND THAWED WHILE SATURATED WITH WATER.

	Length of Bar Mm.	
1. Immersed in water, at room temperature	102.828	
2. Frozen, at 5° F.		102.812
3. Immersed in water, at room temperature	102.823	
4. Frozen, at 6° F.		102.815
5. Immersed in water, at room temperature	102.825	
6. Frozen, at 9° F.		102.816
7. Immersed in water, at room temperature	102.824	
8. Frozen, at 23° F.		102.821
9. Immersed in water, at room temperature	102.825	

The total amount of water in the bar was probably about 11.0 per cent and two-thirds of it was in such a state that it would evaporate in dry air. The bar of lime mortar noted above containing 15.1 per cent of capillary water expanded 0.085 per cent on cooling to 27° F. but this bar of neat cement actually contracted slightly. The bar was six years

[11] *Concrete* **26**, 157-161 (1925).

old when tested and had been soaked two months in water just prior to the freezing tests so that there were no empty capillaries into which the ice formed could expand without causing an external stress. The explanation might be that the water was under such high compression that its freezing point had been lowered below 5° F. or that the water was already in the solid state before it was frozen.

Conclusion.—Portland cement clinker on hydration forms products some of which are crystalline and some of which form a stiff gel. This gel absorbs and gives up water with changing humidity of the air. A bar of neat cement may change in length more than 0.1 per cent with alteration in atmospheric humidity. The linear expansion when changed from dry air to water will be greater than this and may be as great as 0.5 per cent. The gel retains this reversibility at atmospheric temperature for at least twenty years, and there is nothing to indicate that it may not continue indefinitely. The magnitude of the expansion increases with the number of alternations between the dry and the wet state, due to the progressive hydration of particles of unchanged clinker. When a bar of hardened cement is transferred from dry air to benzene, the capillaries become slowly filled with benzene with resultant increase in weight and apparent specific gravity, but without any change in the length of the bar. When the same bar, after evaporation of the benzene, is transferred to water, the capillaries become filled with water with a resultant increase in weight, apparent specific gravity and length. The volume of water adsorbed may be three times as great as that of the benzene absorbed in the prior test. If it be assumed that the benzene filled the larger capillaries and that the surplus volume of water was all adsorbed in the micropores, the increase in volume of the bar should give a measure of the compressed volume of the water. An assumption of this sort indicates that the water was compressed to half its volume, but the figure cannot be given much weight because of the uncertainties as to the amount of air remaining in the capillaries on immersion in benzene and in water respectively. So also the increase in apparent specific gravity cannot be given much weight in computing pressures. Freezing tests on bars of well hardened neat cement saturated with water fail to show any expansion although the bars contain about 11.0 per cent of water of which two-thirds is in such a form that it will evaporate in dry air and be absorbed again on immersion in water. In fact the bars of cement shrink to a greater degree than cast iron as the temperature drops further below the freezing point. This failure to expand at the freezing point may indicate a very high compression of the water or it may indicate that the water was already in the solid state before it was frozen.

The pressures due to adsorption are mainly internally directed, but they do produce a deformation of the bar. The modulus of elasticity of hardened cement mortar is low and hydrated cement is somewhat plas-

tic. A compressive stress of about 5000 pounds to the square inch will produce rupture of even the best concrete. The disintegration of concrete exposed to the weather is largely due to the expansion and contraction of the colloidal material coupled with the progressive expansion due to the hydration of fresh portions of cement clinker with each long immersion in water.

Department of Chemical Engineering,
University of Michigan,
Ann Arbor, Michigan.

EFFECT OF ELECTROLYTES ON ELECTROENDOSMOSE THROUGH WOOD MEMBRANES

BY ALFRED J. STAMM [1]

Previous investigations by the author on electroendosmose through wood membranes [2] were undertaken chiefly as a means of studying the capillary structure of wood. Pure distilled water was the liquid used in all of the experiments, and its rates of flow through sections of different species of wood of varying thickness cut in each of the three different structural directions were examined. In the investigation here reported various aqueous solutions were used, and the rates of electroendosmose were determined through transverse sections less than a single fiber length in thickness (0.1 to 0.25 cm.). In all cases a considerable proportion of the fibers were cut across twice, giving the membranes a total effective capillary cross section of 100,000 to 200,000 capillaries per sq. cm., of approximately 0.0025 cm. average diameter.

Wood membranes lend themselves readily to a study of the effect of electrolytes on electroendosmose as the same membrane, by removal and washing, can be used for a number of experiments, thus avoiding any error that might be introduced by assuming that the structure of different sections is uniform. Further, any slight permanent chemical changes of the wood surface caused by various chemical reagents can be readily detected by determining the velocity of electroendosmose of pure distilled water through the membrane before and after treatment, the removal of the free chemical being assured by conductivity and pH measurements.

The apparatus and the technique used were the same as previously described.[2] No effort was made to convert the results to a contact potential basis except in the case of pure distilled water. This conversion seemed futile not only because of the uncertain effect of electrolytes on the effective viscosity and dielectric constants at solid-liquid interfaces, which may differ materially from those of pure bulk solutions, but also because of the present uncertain status of the Helmholtz double-layer theory in its relationship to the phenomenon of electroendosmose.[3]

Wood is negatively charged with respect to distilled water, as is indicated by the fact that the direction of passage of the water through

[1] Associate Chemist in Forest Products, U. S. Forest Products Laboratory, Madison, Wis.
[2] "Colloid Symposium Monograph," 4, 246 (1926).
[3] McBain, *J. Phys. Chem.*, 28, 706 (1924); Usher, *Trans. Faraday Soc.*, 21, 406 (1925); McBain, "Colloid Symposium Monograph," 4, 18 (1926); Burton, *idem.*, p. 132.

its capillaries is always from anode to cathode. Bethe and Toropoff[4] have made similar observations. The addition of acids and alkalies is ineffective in reversing the charge (direction of flow). Figure 1 shows

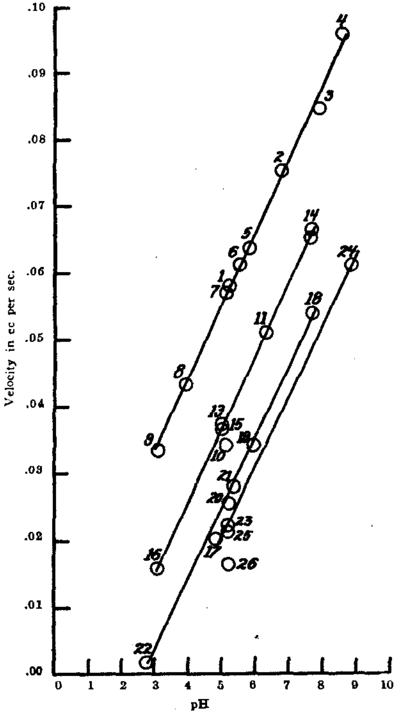


FIG. 1.—Effect of pH on velocity of electroendosmose.

the effect of variations in sodium hydroxide and hydrochloric acid concentrations expressed in terms of pH upon the rate of electroendosmose through a transverse section of Alaska cedar (thickness 0.112 cm.).

[4] *Z. phys. Chem.*, 89, 597 (1915).

The pH was determined on a composite sample of the aqueous solution taken from both electrode chambers just after making each determination. The experimental points in the figure are numbered to indicate the order in which the changes in pH were made. The distilled water used had a specific conductivity of 5×10^{-6} mho and a pH of 5.4.

The range of pH investigated was rather narrow owing to the fact that excessive electrolysis took place at higher concentrations, making the determinations uncertain. There were indications of a break in the curve (decrease in velocity of electroendosmose with increase in pH) occurring around pH = 10, but owing to the electrolytic effect the results of a series of experiments over a narrower range of pH are given.

An addition of sodium hydroxide increased the rate of electroendosmose, and its subsequent removal by washing decreased the rate to the same extent. An addition of hydrochloric acid decreased the rate, whereas its removal caused a permanent shift in the rate. Subsequent addition of alkali caused an increase in rate as before, but the total rate was depressed by a constant subtractive amount. The above cycle was repeated several times and each time a further permanent decrease in rate of electroendosmose was found upon removal of the acid. After obtaining the point numbered 25, the membrane was soaked in 6*N* hydrochloric acid for two days, after which it was washed with distilled water until the pH was that of the wash water. The rate of electroendosmose was again determined giving point number 26.

The fact that the membrane can be completely restored to the original rate of electroendosmose after removing sodium hydroxide shows that the alkali has no permanent effect upon the wood at the concentrations used. The adsorption or hydration is either entirely reversible or is ineffective in changing the contact potential of the wood against water. This is not the case with wood previously treated with hydrochloric acid, as is evidenced by the permanent reduction of the rate of electroendosmose. The potential gradient E across the membrane remained constant at 108 volts per cm., within the accuracy of the experimental measurements. The only other factor in the classical electroendosmose equation [5] besides that of the contact potential P that it seems could have possibly caused the change in the velocity, V, is a change in the total capillary cross section q. In order to account for a decrease in V, q would have to decrease as a result of the action of the acid. This, however, would require an unreasonable extent of shrinkage. It seems most probable, then, that the major part of the reduction of the rate of electroendosmose is caused by a reduction of the contact potential. Acids in moderate concentration are known to cause hy-

[5] $P = (300)^2 \frac{4\pi\eta V}{EDq}$, where P is the contact potential in volts, η the absolute viscosity of the liquid. V the velocity of electroendosmose in cc. per second, E the potential gradient through the membrane in volts per cm., D the dielectric constant of the liquid, and q the total capillary cross section of the membrane in sq. cm.

drolysis of the cellulose and other carbohydrates of the wood. Very likely partial hydrolysis took place even at the low concentrations of the above experiments. The intermediate hydrolysis products formed on the surface of the wood thus seem to have a smaller contact potential against water than has the original wood. On the other hand, there is no evidence of any definite chemical action of dilute solutions of sodium hydroxide upon extractive-free wood or cotton cellulose. X-ray spectrographs[6] indicate that only at higher concentrations (12 to 15 per cent) does sodium hydroxide have an effect upon the diffraction patterns. The effect at lower concentrations seems to be only that of hydration. The above experiments thus indicate that a sensitive method of detecting a definite chemical action on the surface of the wood is offered by determining electroendosmotically if the rate of flow and subsequently if the contact potential is permanently altered.

Harrison's[7] experiments on streaming potential, using cotton cellulose, are well in accord with the above results, though he gives no data which would show the permanent shift caused by the action of dilute acids. The initial effects, however, of increasing acid and alkali concentrations are very similar to those given in this paper. Harrison obtained 0.0157 volts as the contact potential of cotton against distilled water, whereas the average value for wood, previously determined by the author[2] is 0.0136 volts. Harrison also found the contact potential to vary directly as a function of the logarithm of the concentration, which is equivalent to obtaining a straight-line relationship between the contact potential and the pH. Assuming the potential gradient to be constant over the pH range studied, and the classical electroendosmose equation to be valid, the same relationship is obtained for the above results. Perrin[8] found that alkalies increase the rate of electroendosmose through cotton cellulose and that acids decrease it. No reversal of direction of flow resulted from concentrations of hydrochloric acid as high as $\frac{1}{30}$ N. Bethe and Toropoff[4] similarly found that no reversal in direction of electroendosmose could be obtained for wood, colloidian or charcoal with acids and alkalies, all being negatively charged towards the solutions at all times.

The results of this investigation as well as the others cited, indicate that if cotton cellulose and wood show an isoelectric point with acid or alkali, it exists at a relatively high acid concentration. As the acid has quite an appreciable effect upon cellulose and wood at these concentrations, any determined isoelectric point would be meaningless.

The permanent effect of several concentrated solutions of acids and bases upon the rates of electroendosmose of distilled water through wood membranes was determined. Sections were soaked in $6N$ solu-

[6] Katz and Vieweg, *Z. Elektrochem.*, 31, 157 (1925).
[7] *J. Soc. Dyers Colourists*, 27, 279 (1911); *Trans. Faraday Soc.*, 16, 116 (1920).
[8] *J. chim. phys.*, 2, 601 (1904).

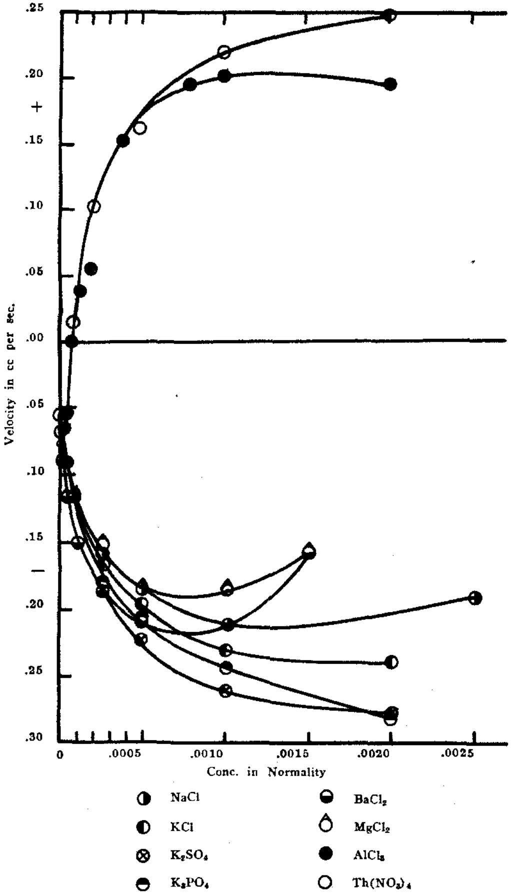


FIG. 2.—Effect of salts on velocity of electroendosmose.

tions of the acids and bases for two days after determining the rates of electroendosmose with distilled water. The membranes were then washed until the pH was that of the wash water, and the rates of electroendosmose were again determined. Table 1 gives the fraction of the original rate obtained in each case. The potential gradient E through the membranes was not affected by the treatment.

TABLE 1.—PERMANENT REDUCTION IN RATE OF ELECTROENDOSMOSE CAUSED BY TREATMENT OF THE MEMBRANES WITH 6N SOLUTIONS OF ACIDS AND BASES.

	Rate After Treatment / Rate Before Treatment	Membrane Color After Treatment
Hydrochloric Acid	0.283	Brownish black
Nitric Acid	.102	Bright yellow
Acetic Acid	.760	Yellow brown
Sodium Hydroxide	.220	Dark brown
Ammonium Hydroxide	.523	Almost black

This table shows that not only acids cause a permanent reduction in the rate but strong bases have the same effect. This is in accord with the results of Harrison [7] on cotton cellulose. He found a permanent reduction of contact potential upon mercerizing with both sodium hydroxide and nitric acid.

The effect of salts upon the rate of electroendosmose is given in Figure 2. In all cases the membrane could be brought back to the original rate by washing for some time with distilled water. After making the determinations with thorium nitrate, it took ten days washing to remove all of the salt, but in the other cases the time was considerably less. The rate of electroendosmose increased with an increase in concentration for salts having univalent and divalent cations. The maxima for the divalent cation salts were obtained at a lower concentration than for the univalent cation salts. An increase in the valency of the anion increased the rate of electroendosmose somewhat, and presumably increased the concentration at which the maxima occur, though the concentrations could not be increased sufficiently to obtain these maxima. Aluminum chloride, with a trivalent cation, increased the rate very slightly for extremely low concentrations (0.00002 N) then caused a decrease in rate. At 0.0001 N the rate became zero and above this concentration the passage of water through the membrane was in the opposite direction, indicating a reversal of contact potential from negative to positive. In no case was absolutely zero motion secured. On closing the circuit, the indicator bubble,[9] for cases of practically no contact potential, moved extremely slowly with a negative acceleration, then stopped, and slowly accelerated in the opposite direction. This self-reversal was very likely due to polarization at the electrodes. Thorium nitrate with a tetravalent cation gave a similar slight increase in rate at 0.00002 N

[9] Stamm, *loc. cit.*

and a zero rate at 0.00008 *N*. With higher concentrations of aluminum and thorium salts the rate of electroendosmose increased in a similar manner, and to about the same extent as the other salts had caused it to increase in the opposite direction. These results are well in accord with results from similar electroendosmose, streaming potential, and cataphoresis studies with other materials. Powis [10] found similar effects of ions with different valencies upon the contact potential between oil drops and water by cataphoresis studies. Kruyt [11] and Freundlich and Rona [12] obtained the same type of effect of electrolytes on the streaming potential through glass capillaries, and Elissafoff [13] on electroendosmose through glass and quartz capillaries. More recent papers by Fairbrother and Mastin,[14] Remy,[15] and Hepburn [16] show the effect of electrolytes on electroendosmose through various membranes. In all cases of negatively charged membranes, it is the polyvalent cations (greater than a valence of two) that are effective in reversing the charge. Polyvalent anions tend to increase the negative charge. The maxima for divalent cations occur at lower concentrations than for univalent cations. The maximum velocities of flow and contact potentials seem to be of about the same order of magnitude for the higher concentrations of salts regardless of whether positive or negative. The concentrations of aluminum and thorium salts with monovalent anions necessary to reduce the velocity of electroendosmose and the contact potential to zero are higher for wood (0.0001 and 0.00008 *N*, respectively) than for carborundum [17] (0.00001 and 0.000007 *N*, respectively), and lower than for cylinder oil [18] (0.0024 and 0.0012 *N*, respectively). The wood membranes are thus shown to follow the normal effect of electrolytes on material with a negative contact potential, and though acted upon chemically by dilute acids and more concentrated bases, the effects are entirely of the type that would be expected.

Summary

1. Dilute alkali solutions increase the rate of electroendosmose through wood membranes, and dilute acid solutions decrease it in such a way as to give a straight-line relation between rate and pH.

2. Dilute acids affect the membrane permanently, perhaps causing hydrolysis on the internal surface, in such a way as to reduce the rate of flow.

3. Concentrated acids and bases both permanently reduce the rate of electroendosmose.

[10] *Z. physik. Chem.*, 89, 91 (1915).
[11] *Kolloid Z.*, 22, 81 (1918).
[12] *Sitzungsber. Preuss Akad. Wiss.*, 20, 397 (1920).
[13] *Z. physik. Chem.*, 79, 385 (1912).
[14] *J. Chem. Soc.*, 125, 2319, 2495 (1924); 127, 322 (1925).
[15] *Z. Phys. Chem.*, 118, 161 (1925).
[16] *Proc. Phys. Soc. (London)*, 38, 363 (1926).
[17] Fairbrother and Mastin *loc. cit.*
[18] Powis, *loc. cit.*

4. Aqueous salt solutions show the normal effect of salts with different valent cations and anions on negatively charged membranes. Tri- and tetravalent cations cause a reversal of the direction of flow and of the sign of the contact potential. Polyvalent anions increase the rate of flow and the negative contact potential. Divalent cations cause a maximum in the rate of flow at a lower concentration than for univalent cations. Trivalent cations cause a maximum in the rate of flow at a lower concentration than for tetravalent cations. Tetravalent cations cause the reversal in the direction of flow at a lower concentration than the trivalent cations.

Forest Products Laboratory,
Madison, Wisconsin.

THE PHYSICAL CHEMISTRY OF COLOR LAKE FORMATION

By Harry B. Weiser and Everett E. Porter

The adsorption of many dyes by wool, silk, and cotton is so weak that they are of value to the practical dyer only when used in connection with mordants. The term mordant (from mordre, to bite, or to corrode) was first applied by the French to metallic salts which were supposed to act by biting or opening up a passage into the fibers of the cloth giving access to the color. Thus alum was believed to be effective in fixing certain dyes, owing to the solvent or corrosive action of the sulfuric acid. It is now known that the real mordant is the hydrous oxide and not the acid derived from the salt.

In general, a mordant may be defined as any substance that is taken up strongly by the fiber and in turn takes up the dye strongly. Two classes of mordants are generally recognized; acid, and basic or metallic. The acid mordants are the tannins, the fatty acids, albumin, hydrous silica, arsenic acid, and phosphoric acid, while the basic mordants are the hydrous oxides of the heavy metals, the most important of which are the hydrous oxides of chromium, aluminum, iron, tin, and copper in the order named.

In dyeing a mordanted cloth, it is in most cases the mordant rather than the fiber which takes up the dye. When a dye is taken up by a mordant in the absence of a fiber, the complex is called a color lake.

This investigation deals with the mechanism of the formation of color lakes of the hydrous oxides. For a long time all such color lakes were believed to be definite chemical compounds between the dye and the mordant. This view was questioned by Biltz and Utescher [1] who investigated the behavior of alizarin with the hydrous oxides of chromium and iron. With the former, the amount of dye taken up increased continuously with increasing concentration of solution, giving no indication whatsoever of the formation of chromium alizarate. With hydrous ferric oxide, on the other hand, the amount of dye taken up increased so rapidly with relatively small change in the concentration of the bath, that Biltz was led to assume the formation of a ferric alizarate. More recently Bull and Adams [2] investigated the iron-alizarin lake and concluded that it is a ferric oxide-sodium alizarate complex.

[1] *Ber.*, **38**, 4143 (1905).
[2] *J. Phys. Chem.*, **25**, 660 (1921).

Marker and Gordon[3] studied the influence of hydrogen-ion concentration on the amount of the basic dyes, crystal violet and methylene blue, and the acid dyes, orange II and metanil yellow, taken up by ferric oxide, alumina, and silica. In most instances breaks were obtained in the pH-adsorption curves which were interpreted to mean that chemical compounds were formed between the hydrous oxides and the dyes investigated. As we shall see, the value of Marker and Gordon's paper would seem to lie chiefly in their recognition of the importance of hydrogen-ion concentration in color lake formation rather than in the data submitted or the conclusions drawn therefrom.

In the light of our observations[4] on adsorption of ions from a mixture of electrolytes it would seem that the concentration of the ions present in the dye bath, including hydrogen and hydroxyl, might be quite as important in determining the composition of a color lake as the concentration of the dye itself. Moreover, the nature, physical character, and purity of the mordant would be expected to influence the composition of the lake. In order to determine the effect of each of the several factors on the lake-formation process, the first investigations were made on systems in which all the variable constituents could be determined quantitatively. To simulate the conditions of lake formation as nearly as possible, observations were made at varying hydrogen-ion concentrations on the taking up of the inorganic anion, sulfate, and the organic anion, oxalate, both separately and simultaneously, by highly purified hydrous oxides of known composition. The observations were then extended to include the true color lakes.

Experimental Procedures

The Adsorbent.—In most of the earlier investigations on adsorption of the dyes by the hydrous oxides, the latter were precipitated from the respective salt solutions with ammonia, washed by decantation, and dried. A weighed amount of the adsorbent prepared in this way was shaken with the dye and the amount taken up was determined from the change in the concentration of the solution. This method of procedure is open to certain objections: First, it is impossible to obtain equilibrium conditions in a reasonable length of time; second, it is impossible to get absolutely uniform samples; and third, the purity of the oxides is uncertain.

To obviate these difficulties the hydrous oxides used in the present investigation were prepared in the form of sols. This was done by precipitating the gels from the respective chloride solutions with ammonia, washing by decantation with the aid of the centrifuge until peptization began, and finally, peptizing with the smallest possible

[3] *Ind. Eng. Chem.*, 16, 1186 (1924); 15, 818 (1923).
[4] Weiser, *J. Phys. Chem.*, 30, 20, 1527 (1926).

quantity of hydrochloric acid. The sols formed in this way were dialyzed in boiling solution for approximately one hundred hours according to the method of Neidle,[5] using a five-liter balloon flask to replace the open beaker. The rate of flow of water was kept at about two liters per hour. By this procedure, products were obtained having a much higher degree of purity than the precipitated gel.

Determination of Adsorption.—Two methods may be employed for determining the adsorption by the gel thrown down on the addition to the sol of a given amount of electrolyte: The gel may be washed by the aid of the centrifuge and the analysis made on the supernatant liquid with all the wash water; or an aliquot part of the supernatant liquid may be pipetted off and analyzed, calculating the adsorption from the change in concentration. From the results of a number of preliminary experiments it was found that the latter method gives more reliable and consistent results. The errors eliminated by using this method are the differences in the conditions of washing and the variation in the reversibility during washing. The latter factor is especially important since the adsorption is reversible in all cases, equilibrium between the wash water and the precipitate being established more or less rapidly. The error introduced by the failure to take into account the volume occupied by the solid is kept small, amounting to less than one tenth of one per cent in most cases. The fact that this error is constant in any series of experiments, reduces still further any objection to the method.

The mixing of the hydrous oxide sol with the electrolyte was done in 250 cc. wide-mouth bottles with ground-glass stoppers. The solution to be mixed with the sol was put in the bottle and diluted to exactly 150 cc. Fifty cubic centimeters of sol containing the desired amount of hydrous oxide was placed in a 60 cc. bulb with a large neck, inserted through a rubber stopper which fitted the bottle. In order to retain the sol when the bulb was inverted, the neck of the latter was fitted with a thin slice of rubber cut from a stopper. To mix the solutions, the stopper, with the bulb, was inserted in the bottle, which was given a quick jerk, thereby dislodging the thin stopper from the neck of the bulb and allowing very rapid and thorough mixing of the solutions. Numerous tests showed that equilibrium between the adsorbent and the adsorbate was established almost at once. However, the mixtures were allowed to stand in the glass stoppered bottles for about 24 hours, after which they were centrifuged and an aliquot part withdrawn for analysis. The hydrogen-ion concentration was determined in the supernatant liquid as well as in a similar mixture in which water was substituted for the sol. The former determinations are designated in the tables as "pH after adsorption" and the latter as "pH before adsorption." Since the sol is approximately neutral, if the small error introduced

[5] *J. Am. Chem. Soc.*, **29**, 71 (1907).

by the space occupied by the solid particles of the oxide is neglected, the difference between the two pH values is the change due to the adsorption by the colloidal particles.

Hydrogen-Ion Concentration.—The hydrogen-ion concentrations were measured throughout with the hydrogen electrode. The apparatus employed was the Leeds and Northrup "Type K" potentiometer in connection with one of their sensitive galvanometers. A small electrode vessel of special design requiring but 4 cc. of solution for a determination was used. The gas entered the electrode vessel at the bottom through a very small capillary, a pressure of seven to eight centimeters of mercury being required to cause a flow of one cubic centimeter of gas each three seconds. This served to agitate the liquid very effectively without blowing it out of the vessel. The electrodes were prepared by platinizing 4 millimeter glass tubes to a height of 1 centimeter. These electrodes come to equilibrium more quickly than the platinized platinum electrodes and are easily and economically renewed. The hydrogen used was purified by conducting it over hot platinized asbestos, bubbling through potassium hydroxide, sulfuric acid, and finally through water at the same temperature as the electrode vessel.

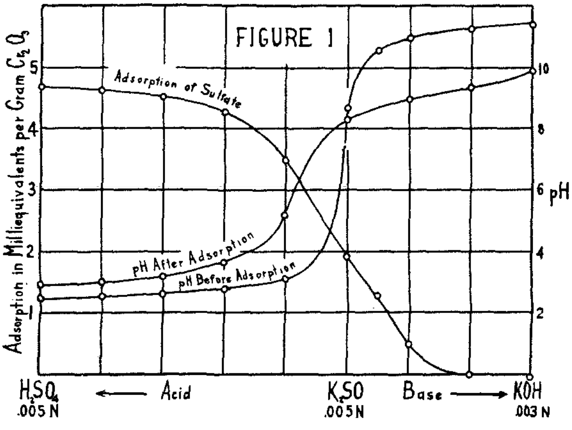
Adsorption of Sulphate and Oxalate

The Adsorption of Sulfate.—Observations with hydrous chromic oxide as adsorbent will serve to illustrate the results obtained. The adsorption of sulfate by a constant amount of the hydrous oxide at varying hydrogen-ion concentrations, typifies the results obtained with other multivalent ions. In all the experiments, the initial sulfate concentration was maintained constant at 0.005 normal, while the pH value was varied through wide limits using suitable proportions of sulfuric acid, potassium sulfate, and potassium hydroxide. Obviously, this procedure introduces varying amounts of potassium ion as well as of hydrogen and hydroxyl ions. This effect may be considered as negligible, since it was found in some experiments to be recorded in a later section, that very little or no alkali ion is adsorbed under similar conditions. If the alkali adsorption were appreciable it would serve to increase the adsorption of the negative ions. It should be pointed out that the same initial concentration of sulfate leads to a varying equilibrium concentration. Since the final concentration is smaller the greater the adsorption, it follows that the variations in the adsorption values would have been somewhat larger than those observed if the final concentration had been kept constant. However, the final concentration is sufficiently large in all cases to put the adsorption well on the flat of the isotherm.

The marked effect of the hydrogen and hydroxyl ions on the adsorption of sulfate is shown by the data recorded in Table 1 and

TABLE 1.—ADSORPTION OF SULFATE BY HYDROUS CHROMIC OXIDE AT VARYING pH VALUES.

Cc. of Soln. Mixed with 50 Cc. of Sol Containing 0.125 Grams of Cr_2O_3 in a Total of 200 Cc.			Adsorption Values, Milli-equiv. per Gram Cr_2O_3	pH Values	
$N/50$ H_2SO_4	$N/50$ K_2SO_4	$N/50$ KOH		Before Adsorption	After Adsorption
50	0	0	4.66	2.42	2.87
40	10	0	4.60	2.49	2.97
30	20	0	4.52	2.59	3.15
20	30	0	4.28	2.73	3.64
10	40	0	3.48	3.09	5.15
0	50	0	1.90	8.68	8.29
0	50	5	1.28	10.61	8.73
0	50	10	0.48	10.95	8.96
0	50	20	0.08	11.28	9.39
0	50	30	0.10	11.41	9.87



shown graphically in Figure 1. It will be seen that raising the concentration of the hydrogen ion increases the positive charge on the particles, thereby increasing their capacity to adsorb sulfate. The adsorption of the sulfate falls off quite rapidly with increasing concentration of the hydroxyl ion, the carrying down of the sulfate being completely nullified at a pH value of about 9.2. It is obvious, however, that both sulfate and hydroxyl are adsorbed in the alkaline range

from a pH of 7 to 9. In Loeb's investigations on the proteins[6] it seems probable that he overlooked the specific effect of cations other than hydrogen and of anions other than hydroxyl since he worked with relatively low concentrations of salts.

The pH-adsorption curve is smooth throughout showing no indication of the formation of a compound between the sulfate and the hydrous oxide even at pH values as low as 2.0.

Simultaneous Adsorption of Sulfate and Oxalate.—Observations on simultaneous adsorption by hydrous oxides have been made by Mehrotra and Sen[7] and by Miller.[8] The former studied the mutual effects of copper and barium in varying proportions on their relative adsorption by hydrous manganese dioxide. Since no account was taken of the hydrogen-ion concentration to which hydrous manganese dioxide is quite sensitive, their results are of questionable value. Data in one specific case led them to the general conclusion that "The sum of the adsorption of two ions from a mixture is always greater than the adsorption of either of them present alone in the solution." It has been shown conclusively[9] that this is not true in every case, and it may not be true in any case provided the precipitations take place under the same conditions.

Miller studied the simultaneous adsorption of sulfate and oxalate by alumina and arrived at the conclusion that the adsorption was a solid solution phenomenon since the concentration of sulfate (or oxalate) in the solution divided by its concentration in the adsorbent was a constant. This conclusion is not justified since the maximum value for the alleged constant was over a thousand times the minimum value. Moreover, even if these values had been constant, his data would not have justified the conclusion since the hydrogen-ion concentration was allowed to vary through wide limits and this is the determining factor in the particular range of variation that Miller happened to get. It should be noted further, that as the ratio of total sulfate to oxalate falls off, the value for the sulfate constant increases, the increase being very rapid as equal concentrations of sulfate and oxalate are approached. Had Miller taken ratios of oxalate to sulfate greater than one, the so-called constant for sulfate would have been found to approach infinity very rapidly, for in a neutral solution the adsorption of sulfate becomes zero in the presence of an appreciable excess of oxalate. This is illustrated by some comparable observations on the simultaneous adsorption of sulfate and oxalate by hydrous chromic oxide, recorded in Table 2. In these observations the adsorption of 25 cc. of the $N/50$ solution corresponds to 1.77 milli-equivalents per gram of chromic oxide. Since the precipitation concentrations as well as the adsorptions of oxalate

[6] "Proteins and the Theory of Colloidal Behavior."
[7] *J. Indian Chem. Soc.*, 3, 297 (1926).
[8] *U. S. Public Health Repts.*, 30 1502 (1924).
[9] Weiser and Porter, *J. Phys. Chem.*, 31, 1383 (1927).

TABLE 2.—ADSORPTION BY HYDROUS CHROMIC OXIDE FROM MIXTURES OF OXALATE AND SULFATE.

Cc. of Soln. Mixed with 50 Cc. of Sol Containing 0.283 Grams of Cr_2O_3 in a Total of 150 Cc.		Adsorption in Milli-equiv. per Gram of Cr_2O_3			
$N/50\,K_2C_2O_4$	$N/50\,K_2SO_4$	Oxalate	Sulfate	Total	pH After Adsorption
50	0	2.13	0.0	2.13	8.30
60	0	2.17	0.0	2.17	8.37
50	25	2.09	−0.03	2.06	...
50	50	2.04	0.14	2.18	8.11
25	50	1.45	0.46	1.90	7.68
10	50	0.65	1.30	1.95	7.49
0	50	0.00	1.86	1.86	7.32
25	25	1.63	0.36	1.99	7.97

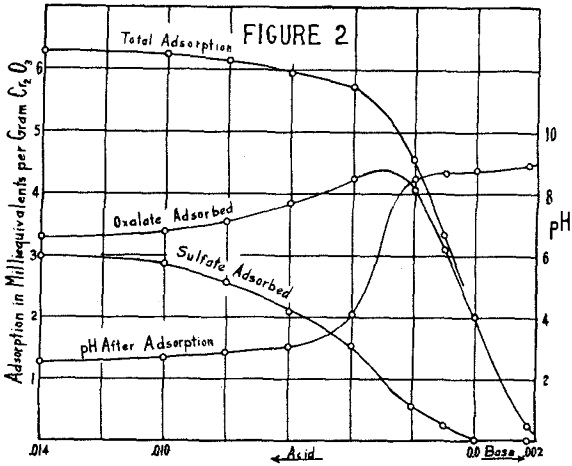
and sulfate are so nearly equal, one might be led to conclude that their adsorptions would be nearly equal when both are present in the same solution. This is not even approximately true if the solution is neutral or basic. In order to get any measurable quantity of sulfate adsorbed at a pH of 8 it is necessary to have a very low concentration of oxalate, and to get equivalent adsorptions at this pH value the final concentration of sulfate must be approximately 128 times that of oxalate. The conclusions to be drawn from these data are: First, under the same conditions the equivalent adsorption by the hydrous chromic oxide is approximately equal whether it be all sulfate, all oxalate, or some of each. Second, so long as there is an excess of oxalate in the bath it displaces the sulfate almost completely while an excess of sulfate has but little effect on the adsorption of oxalate. Third, it is necessary to limit the concentration of the oxalate in order to make a study of the simultaneous adsorptions of oxalate and sulfate in a neutral or basic solution.

To determine the effect of varying hydrogen-ion concentration in the simultaneous adsorption, a total quantity of oxalate plus sulfate corresponding to 16 milli-equivalents per gram of oxide was used through-

TABLE 3.—REPLACEMENT OF OXALATE BY SULFATE AT LOW pH VALUES.

Cc. of Soln. Mixed with 50 Cc. of Sol. Containing 0.125 Grams of Cr_2O_3 in a Total of 200 Cc.						Adsorption in Milli-equiv. per Gram of Cr_2O_3			
0.037*N* KOH	*N*/50 K_2SO_4	*N*/50 H_2SO_4	*N*/50 $K_2C_2O_4$	*N*/50 $H_2C_2O_4$	*N*/25 HCl	Oxalate	Sulfate	Total	pH of Mixture
10	50	0	50	0	0	0.23	0.01	0.22	8.91
0	50	0	50	0	0	2.01	0.01	2.00	8.80
0	40	10	50	0	0	3.12	0.25	3.37	8.68
0	30	20	50	0	0	4.04	0.53	4.57	8.51
0	10	40	50	0	0	4.25	1.54	5.79	4.06
0	0	50	40	10	0	3.81	2.09	5.90	3.06
0	0	50	20	30	0	3.56	2.56	6.12	2.85
0	0	50	0	50	20	3.37	2.85	6.22	2.72
0	0	50	0	50	20	3.31	2.96	6.27	2.59

out the series of observations. In actual quantities of reagents this is represented by sufficient sol to contain 0.125 grams of oxide and 50 cc. of each of the $N/50$ solutions. The concentrations are sufficiently high so that at maximum adsorption the bath will not be exhausted with respect to either sulfate or oxalate ion. The results are given in Table 3 and shown graphically in Figure 2. The form of the adsorption curves show: *first, that the oxalate is displaced appreciably by the* sulfate when the final solution is but faintly acid, and second, that



the adsorptions approach equivalence in the strongly acid solution. This observed behavior is probably not due to a shift in the relative adsorbability of the bivalent oxalate and sulfate ions but is due to the relatively greater conversion of bivalent oxalate to the less strongly adsorbed bioxalate ion than of the bivalent sulfate to bisulfate ion in the acid solution. In the section on alizarin lakes it will be shown that the behavior of oxalate in this respect is typical of the acid dyes.

Alizarin Lakes

Since alizarin and its derivatives constitute the most important mordant dyes, the mechanism of the formation of alizarin lakes

was first considered. Biltz [10] was the first to suggest that the alizarin lakes might not be definite chemical compounds. Thus with hydrous chromic oxide the amount of alizarin SW taken up increases continuously with increasing concentration of solution showing no indication whatsoever of the formation of chromium alizarate. On the other hand, with hydrous ferric oxide there was a rather marked increase in the amount of alizarin SW taken up with relatively small change in the equilibrium concentration, leading Biltz to conclude that iron and alizarin combine in the ratio of one molecule of Fe_2O_3 to three molecules of alizarin. But the amount of alizarin taken up by the iron oxide is far in excess of that necessary to form alizarate, hence one is confronted by the necessity of assuming either that alizarate adsorbs the excess of dye or that the whole phenomenon is a case of adsorption of the dye by the oxide. Recently the iron and aluminum lakes of alizarin have been investigated in Bancroft's laboratory [11] and the conclusion reached that the lakes are adsorption complexes of sodium alizarate and the hydrous oxides of iron and aluminum respectively. Since this conclusion could not be reconciled with our observations on the taking up of sulfate and oxalate by the hydrous oxides, a systematic investigation of the alizarin lakes and the factors influencing their formation was undertaken.

The Adsorption of Alizarin SW.—The sodium salt of alizarin mono-sulfonate was chosen for the initial experiments for several reasons: It is easy to determine quantitatively even in small amounts; it is not reduced at the hydrogen electrode in dilute solution; its acid is sufficiently soluble that no precipitation takes place throughout a wide pH range; and finally it is readily purified and weighed.

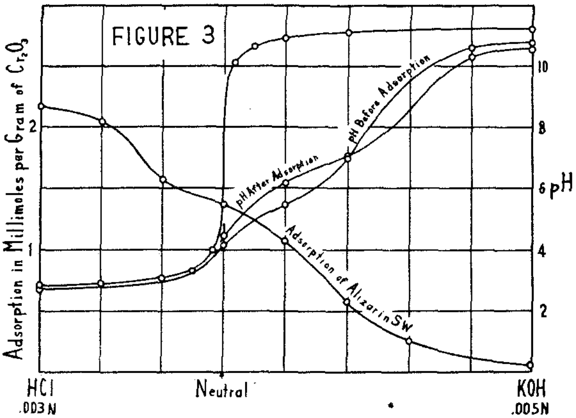
The adsorption of alizarin SW by hydrous chromic oxide at varying hydrogen-ion concentrations was determined by the same general method

TABLE 4.—ADSORPTION OF ALIZARIN SW BY HYDROUS CHROMIC OXIDE AT VARYING pH VALUES.

Cc. of Soln. Mixed with 5 Cc. of Sol. Containing 0.0125 Gram of Cr_2O_3 in a Total of 20 Cc.			Adsorption Value in Millimoles Alizarin SW per Gram Cr_2O_3	pH Values		
0.04 *N* HCl	0.037 *N* KOH	0.01 *N* Dye		Without Dye or Colloid	Without Colloid	Total Mixture
2.5	0	5	2.46	2.86	....	2.419
1.5	0	5	2.40	....	2.400	2.717
1.0	0	5	2.32	....	2.727	2.822
0.5	0	5	2.18	3.11	2.873	3.042
0	0	5	1.70	....	4.173	4.478
0	0.57	5	1.41	10.62	5.490	6.170
0	1.13	5	1.15	....	7.554	7.556
0	2.27	5	0.16	....	10.529	9.283
0	3.39	5	0.09	11.17	10.634	10.445

[10] *Ber.*, 38, 4143 (1905).
[11] Bull and Adams, *J. Phys. Chem.*, 25, 660 (1921); Williamson, *ibid.*, 28, 891 (1924).

of procedure as was used in determining the adsorption of sulfate at varying pH values. The analysis of alizarin was accomplished by oxidation with potassium permanganate[12] under carefully controlled conditions. The data are shown in Table 4 and represented graphically in Figure 3. The pH curve for the acid and alkali alone in the same total quantity of water is also given. The length of a horizontal line drawn from any point on the curve for the pH of the mixture without the colloid to the acid-alkali curve gives the quantity of acid or base reacting with the dye. The adsorption curve is continuous giving no indication of the formation of a compound at any pH value. As



would be expected, there is quite a buffer effect in the titration of the mono-sodium to the tri-sodium salt. Moreover, there is a corresponding holding up of the adsorption-concentration curve in this region. This has two causes: the concentration of the hydroxyl ions is not increasing in proportion to the alkali added; and, at the same time, the concentration of the highly adsorbable dye ions is rapidly increasing. Just as was found in the case of sulfate and of oxalate, hydroxyl ion may completely displace the dye, the latter requiring a slightly higher hydroxyl-ion concentration than the former. This indicates that the dye is more strongly adsorbed than either sulfate or oxalate but is not so strongly adsorbed as hydroxyl.

[12] Weiser and Porter, *J. Phys. Chem.*, **31**, 1824 (1927).

Simultaneous Adsorption of Alizarin and Other Ions.—The addition of sulfate to the acid baths which give up their color too rapidly, has long been followed by the practical dyer. The sulfate by decreasing the adsorption and by retarding the rate of adsorption of the dye anion, tends to give a more even dyeing of the fabric. Sometimes, however, the presence of a very small amount of sulfate is objectionable. Bancroft [13] assumes that the purpose of adding calcium ion as calcium acetate to an alizarin bath is not to give a calcium aluminum alizarate or calcium chromium alizarate of some sort [14] on the mordanted cloth but to remove sulfate ion which cuts down the adsorption of alizarin ion. As will be seen in the next section calcium sulfate is too soluble to enable one to account for the action of calcium ion in this way.

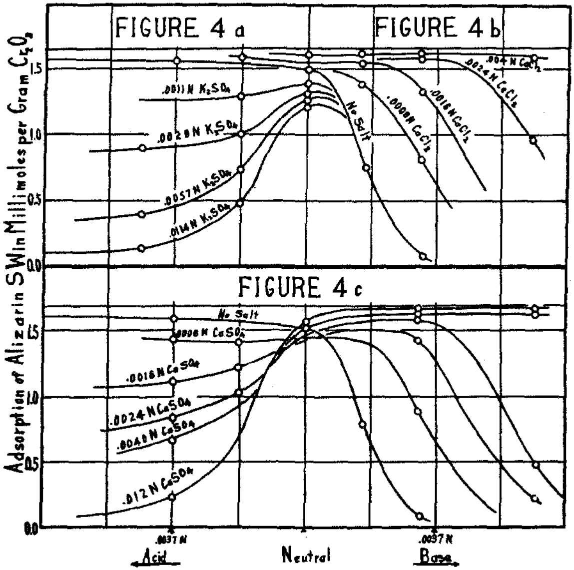
Pelet-Jolivet [15] has demonstrated that readily adsorbed anions such as sulfate and phosphate cut down the adsorption of acid dyes (e.g., crystal ponceau) and readily adsorbed cations such as magnesium increase the adsorption of acid dyes.[16] Davison [17] made some qualitative observations on the effect of sulfate ions and of calcium ions on the adsorption of dyes by fibers as well as by alumina. Thus he finds that 8 grams of Na_2SO_4 in 100 cc. of bath prevents the dyeing of wool by crocine violet. In lower concentrations, the dye is taken up in increasing amounts as the concentration of the sulfate is decreased. Alumina precipitated from aluminum acetate was found to adsorb certain acid dyes, including alizarin, more strongly than that from aluminum sulfate. Calcium acetate was found to increase the adsorption of the acid dye crocine orange but to decrease the adsorption of the acid dye acid green. There are other inconsistencies such as one might expect in qualitative observations.

In the subsequent paragraphs is given the results of quantitative observations on the effect of both sulfate ion and of calcium ion on the adsorption of alizarins by mordants at varying hydrogen-ion concentrations. The observations show clearly the action of neutral salts on color lake formation.

The Effect of Sulfate on the Adsorption of Alizarin SW.—A series of observations was made to determine the effect of sulfate on the adsorption of alizarin SW by hydrous chromic oxide at varying pH values. The method of procedure was essentially the same as was used in determining the effect of sulfate on the adsorption of oxalate. The data are summarized in Figure 4a. Just as in the case of oxalate, it will be noted that the sulfate has little effect on the adsorption of alizarin SW anion in the neutral and basic solutions since, under these conditions, the presence of the much more strongly adsorbed hydroxyl

[13] *J. Phys. Chem.*, 18, 1 (1914).
[14] Liechti, *J. Soc. Chem. Ind.*, 5, 525 (1886).
[15] "Die Theorie des Färbenprozesses," pp. 94, 98, 119, 148 (1910).
[16] Bancroft, *J. Phys. Chem.*, 18, 11 (1914).
[17] *J. Phys. Chem.*, 17, 737 (1913).

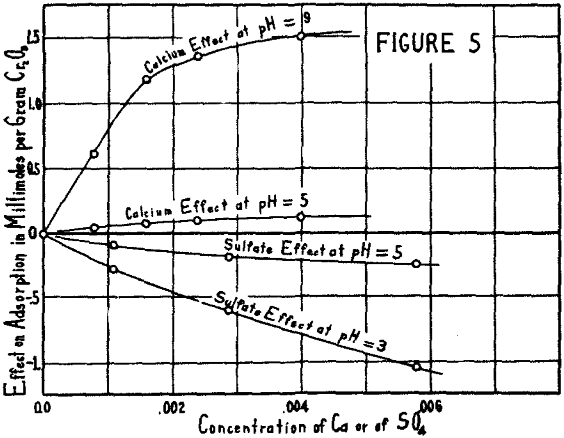
ion masks the relatively small effect of the sulfate. In the acid range, however, the effect of sulfate is quite marked. Since the dye anion is adsorbed more strongly than sulfate from the same concentration, one might expect the latter to have little effect on the adsorption of the former. But the behavior of the dye is similar to that of the oxalate. In the acid solution the effective concentration of the dye becomes



very small due to the suppression of the ionization; and the action of sulfate manifests itself. If the sulfate had been determined in the series of experiments the results would have been similar throughout to those obtained with sulfate and oxalate; viz., sulfate adsorbed more from the acid bath and dye adsorbed more from the neutral and basic bath. Since acid baths are usually employed in dyeing acid dyes, the retarding effect of sulfate is explained even though the dye cation may be more strongly adsorbed than sulfate ion from the same concentration.

The Effect of Calcium Ion on the Adsorption of Alizarin SW.—The results of the observations on the adsorption of alizarin SW in the presence of varying amounts of calcium ion as well as varying hydrogen-ion concentrations are given in Figure 4b. Just as the effect of sulfate ion is small in the presence of the relatively highly adsorbed hydroxyl ion, so the effect of calcium is small in the presence of the relatively strongly adsorbed hydrogen ion.

The Effect of Calcium Sulfate on the Adsorption of Alizarin SW at Varying Hydrogen-Ion Concentrations.—Since the foregoing



experiments show that the effect of the sulfate is large in the acid and negligible in the basic baths and that the effectiveness of the calcium increases with the hydroxyl-ion concentration, one is led to conclude that if calcium sulfate were present, the effect of the sulfate would predominate in the acid solutions and that the influence of the calcium will be unaffected by the sulfate in the basic baths. Direct experimental verification of this conclusion is given by the data plotted in Figure 4c. If the curves *a*, *b*, and *c*, Figure 4 are superimposed it will be seen that *a* and *c* are alike in the acid range while *b* and *c* are alike in the basic range. These data show that the effects of the calcium and sulfate ions in the bath are practically independent of each other and that each is dependent on the hydrogen-ion concentration.

From the above data the effect of sulfate and of calcium on the adsorption of alizarin SW was calculated at different constant pH values with the results shown in Figure 5. It will be noted that the effectiveness of. the calcium approaches zero as the pH value decreases while that of sulfate increases with decreasing pH value.

The Effect of Calcium Ion and Sulfate Ion on the Adsorption of Alizarin.—Observations on the effect of calcium and sulfate ions on the adsorption of alizarin from a sodium alizarate bath are given in

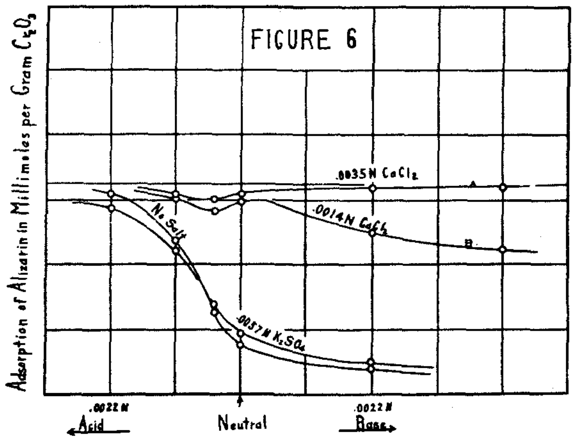


Figure 6. Since the bath must be basic in order for the dye to remain in solution, one would expect the effect of sulfate to be slight, as the observations show. On the other hand, the effect of calcium is marked and increases with its concentration. Hence by the addition of a strongly adsorbed cation one may use a slightly basic bath in which the alizarin is soluble and at the same time avoid the displacement of the dye anion by the hydroxyl. This is the function of calcium ion in the formation of alizarin lakes on the fiber. That the effectiveness of calcium ion is not due to the direct precipitation of alizarin as calcium alizarate is evidenced by the fact that in curve *B*, Figure 6, the quantity of calcium is greater than that of alizarin and yet the dye bath is far from exhausted.

Mechanism of the Formation of Alizarin Lakes.—In the light of the experiments above described, it seemed altogether probable that the alizarin lakes are formed by adsorption of the alizarin anion by the hydrous oxides. It will be recalled that Bull and Adams and Williamson shook up a solution of sodium alizarate with the hydrous oxides and concluded that metallic alizarates were not formed since the hydroxide equivalent to the alizarate was not set free as would happen if a double decomposition reaction took place. The absence of an appreciable quantity of alkali in the bath led to the further conclusion that the lakes are adsorption complexes between the hydrous oxides and sodium alizarate. It was difficult for us to see how this mechanism could be correct for all of our observations showed that when the hydrous oxides are brought in contact with highly ionized salts which yield a strongly adsorbed anion, it is the anion and not the molecule of the salt which is adsorbed. To settle this point the following experiments were carried out:

Pure sublimed alizarin was dissolved in the theoretical amount of sodium hydroxide to give sodium alizarate and the solution diluted to give a $M/100$ solution of the salt. Preliminary experiments were carried out to determine the maximum ratio of sodium alizarate to oxide which could be used and still have a nearly exhausted bath.

For the chromic oxide sol, 113 cc. containing 1.42 grams of Cr_2O_3 was required to decolorize 100 cc. of the sodium alizarate solution. The solutions were mixed in this proportion and 100 cc. of the supernatant liquid was withdrawn and analyzed for sodium; for it was obvious that if the sodium alizarate were adsorbed as the salt, no sodium would remain in the bath. The sodium sulfate was found to be 0.0568 grams. On the basis of equal distribution throughout the mixture, there should have been found 0.0665 grams. Hence more than 85 per cent of the sodium remained in the bath.

For the ferric oxide 237.5 cc. of the sol was mixed with 50 cc. of the $M/100$ sodium alizarate. After mixing, the supernatant liquid was analyzed for sodium as in the previous case and 0.0253 grams of sodium sulfate was found as compared with 0.0284 grams if none were adsorbed. That is, about 90 per cent of the sodium was left in the bath.

For the test on alumina lake, a gel was employed instead of a sol. A solution containing about 7 grams of aluminum chloride was precipitated by the gradual addition of ammonium hydroxide. This was washed by decantation with the aid of the centrifuge until peptization was just started. The matted gel occupied about 60 cc. The addition of 1 cc. of the $M/100$ sodium alizarate caused nearly complete peptization of the gel. When 5 cc. had been added the peptization was complete and the liquid was almost as fluid as water. Cataphoresis experiment on a similar sample showed it to be a negative sol. The addition of more of the sodium alizarate did not have any apparent

effect until the total quantity present was 25 cc. The viscosity increased greatly from this concentration to a total of about 32 cc. More than this started precipitation and when 40 cc. had been added the precipitation was complete. The supernatant liquid was nearly colorless showing that the alizarin was practically all removed in the process. An aliquot part of the supernatant liquid, determined by weight, was analyzed for sodium. It was found to contain 0.0262 gram of sodium as sulfate compared with 0.0271 gram if none had been adsorbed. This shows that nearly 97 per cent of the sodium was left in the bath. If the gels of ferric and chromic oxide had been used it is probable that the amount of sodium remaining in the bath would have been greater than when the highly purified sols were employed. It seems likely that the sodium which is taken up during the precipitation of the sols, is adsorbed as univalent sodium alizarate ions containing one atom of sodium. The pH values of the colorless supernatant liquids showed them to be almost neutral.

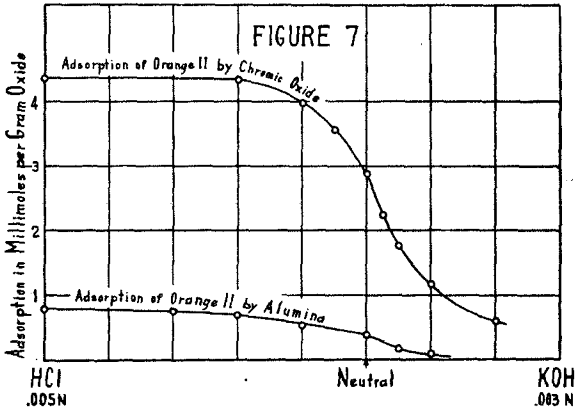
The question naturally arises, how alizarate and hydroxyl ions could be adsorbed by a precipitated gel leaving practically all the sodium in the solution, without imparting a negative charge to the particles. For this to happen, there must be adsorbed along with the hydroxyl and alizarate an equivalent quantity of some positive ion other than sodium or there must be liberated an equivalent quantity of some negative ion. The latter is what happens chiefly since it was found that the sodium is associated with chloride which was present in the gel and was replaced by the more strongly adsorbed hydroxyl or alizarate ions. This suggests that a gel from which practically all the chloride was removed would have a very small capacity for adsorbing anions.

To test this, hydrous chromic oxide was employed since it is the best adsorbent of the oxides of the iron group. The sol containing 1.42 grams of Cr_2O_3 was precipitated with ammonia and washed repeatedly with the aid of the centrifuge, keeping the washing very slightly alkaline with ammonia. By this procedure practically all of the chlorine was removed. After washing the gel it was suspended in a little water to which 0.5 cc. of the $M/100$ sodium alizarate solution was added. After shaking and centrifuging, the supernatant liquid was found to be colored showing that there was little or no adsorption of the dye. On comparing this result with the experiment described above in which 100 cc. of the same dye solution was exhausted by a like amount of the sol, one sees to what extent the adsorption is dependent on the nature and extent of purification of the gel. In the last instance the gel was washed with water containing ammonia; the adsorption capacity of the particles was practically saturated with hydroxyl ions, and therefore the gel could take up but little of the dye anion. In the first experiment, on the other hand, the conditions were exactly reversed. The sol was peptized by acid and even after prolonged dialysis the particles were

positively charged owing to the preferential adsorption of the hydrogen ion. The sol contains an equivalent amount of the less strongly adsorbed chloride ion, a part of which is adsorbed by the particles and the remainder is present in the intermicellar liquid. On adding sodium alizarate the strongly adsorbed alizarate and hydroxyl ions not only neutralize the sol by adsorption but displace the adsorbed chloride ion more or less completely.

Adsorption of Orange II

Observations on the adsorption of orange II by hydrous oxides were made at constant initial pH values and at varying pH values. The re-



sults of the latter observations on the adsorption by hydrous chromic oxide and hydrous alumina are recorded in Figure 7.[1] It will be noted that the adsorption curve is strikingly similar to those obtained with oxalate and sulfate. The orange II is somewhat less strongly adsorbed than either oxalate or sulfate. This might be expected since orange II acts only as the salt of a monobasic acid under the conditions of the experiment. However, the adsorption is quite strong in accord with the usual rule that complex organic ions are adsorbed more strongly than simple inorganic ions of the same valence.

[1] Weiser & Porter, *J. Phys. Chem.*, 31, 1704 (1927).

The Question of Compound Formation.—In view of the fact that the curves representing the amount of orange II taken up by hydrous oxides are continuous both when the initial concentration is left constant while the hydrogen-ion concentration is varied and when the initial hydrogen-ion concentration is kept constant and the dye content varied, there seems little reason to doubt but that the lake formation process is a typical adsorption phenomenon, the composition of the lake depending on the physical character of the hydrous oxide, the concentration of the dye, and the hydrogen-ion concentration of the bath. From similar investigations on the dry gel, Marker and Gordon[18] arrive at the contrary conclusion, that the lake formation process is essentially one of compound formation between the hydrous oxide and the dye at a pH value of approximately 3 where it was believed that the following reaction took place:

$$NaX \xrightarrow{H} HX \xrightarrow{Al_2O_3} AlX_3,$$

where X is the anion of orange II.

The difference in the behavior observed by Marker and Gordon is due primarily to their use of sulfuric acid to control the hydrogen-ion concentration, whereas we employed hydrochloric acid. The use of sulfuric acid was unfortunate. Just as we have seen that the adsorption of sulfate is cut down enormously by the presence of an excess of the more strongly adsorbed oxalate so the adsorption of orange II anion will be cut down by the presence of an excess of sulfate. Moreover, the practical dyer has known for a long time that sulfate ion cuts down the adsorption of acid dyes and we have shown in the case of the alizarin lakes that this effect increases with the concentration of acid in the bath. Accordingly, it is not surprising to find, as Marker and Gordon did, that the adsorption is almost negligible from a pH of 11 to 3.2 in the presence of sulfate ion. But why the sudden increase in the amount thrown down around a pH of 3.0? This is due to the interaction of the acid with orange II to give the corresponding free acid which is only slightly soluble in cold acid solution and hence comes down with the gel. The precipitate is not only not a chemical compound but is not a lake; it is simply an intimate mixture of free orange II acid with hydrous oxide. We did not get a break in the adsorption curve around a pH of 3, since chloride ion does not prevent the adsorption of the dye anion as sulfate does; hence most of the acid dye anion used was adsorbed when the pH value was sufficiently low to give an appreciable concentration of the orange II acid. Moreover, the insoluble acid may tend to form a positive sol in the presence of hydrochloric acid which would not happen in the presence of sulfuric acid.

A further proof of compound formation offered by Marker and

[18] *Ind. Eng. Chem.*, 16, 1186 (1924).

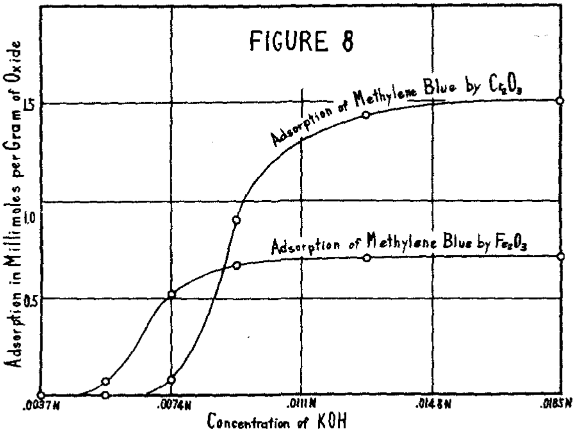
Gordon is that needle-shaped crystals which analyzed for aluminum or iron alizarate were obtained on mixing the respective hydrous oxides with orange II acid. We have found, however, that the product formed in this way either in the hot or in the cold in acid solution or in neutral solution is a mixture of hydrous oxide gel and free orange II acid, the latter imparting the silky, needle-like appearance to the mixture. The composition corresponds to that of a chemical compound only in case the two insoluble substances, the gel and the acid, are mixed in the theoretical ratio and the analysis made for the ratio.

Finally, Marker and Gordon showed that the equilibrium concentration of the dye over the gel in the acid solution was constant and independent of the quantity of dye used. This concentration was 0.04 per cent in the case of the alumina and 0.015 per cent in the case of the ferric oxide gel. The values were assumed to represent the solubilities of the respective salts in the solution. These observations are misleading and the conclusions incorrect. The equilibrium concentration merely represents the solubility of the free acid under the specific conditions of the experiment. The differences are due to a slight variation in the temperature or in the hydrogen-ion concentration, either of which has a pronounced effect.

Adsorption of Methylene Blue

Since methylene blue is a basic dye it was not surprising to find that it is not adsorbed appreciably by the positive sols of the hydrous oxides of the iron group. Figure 8 gives the observations on the adsorption of the dye cation by both ferric and chromic oxides at varying pH values. It was found that, in both cases, the adsorption begins sharply at the concentration of alkali which, in the absence of the dye, starts peptization of the hydrous oxides as negative sols. Above the pH values necessary to start lake formation, the amount of methylene blue adsorbed is a measure of the negative charge introduced by the adsorption of hydroxyl ion; hence it corresponds to the hydroxyl adsorption isotherm. In this connection, it will be noted that the maximum adsorption of methylene blue is obtained in the presence of the same concentration of hydroxyl ion which, in the absence of the dye, gives complete peptization of the oxide as a negative sol. At still higher pH values, the adsorption of methylene blue falls off. A similar behavior in the adsorption of methylene blue by wool was observed by Briggs and Bull [19] who assigned the effect to the increase in the colloidality of the dye in the basic solution. The suppression of the dissociation of the weak base might also be an important factor.

[19] *J. Chem. Soc.*, 121, 2843 (1922); 123, 1318 (1923).



SUMMARY

1. Preliminary to the study of the mechanism of color lake formation, investigations were carried out to determine the effect of hydrogen-ion concentration on the adsorption of an inorganic anion, sulfate, and an organic anion, oxalate, both separately and simultaneously by hydrous oxides which are used as metallic mordants or color bases.

2. Increasing the concentration of hydrogen ion raises the charge on the particles of hydrous oxides, thereby increasing their capacity to adsorb anions. The adsorption of the latter falls off quite rapidly on the alkaline side of the neutral point, being completely nullified at a pH value of about 9.2. However, both hydroxyl and sulfate or oxalate are adsorbed in the alkaline range. In Loeb's investigations on the proteins it seems probable that the specific effects of cations other than hydrogen and of anions other than hydroxyl were overlooked since he worked with relatively low concentrations of salts.

3. A study of the simultaneous adsorption of sulfate and oxalate discloses the fact that the former is adsorbed much more strongly than the latter in the alkaline and neutral range. From the basic solution no measurable quantity of sulfate is adsorbed in the presence of an excess of oxalate. From a neutral solution, the adsorption of sulfate

and oxalate are equal when the ratio of the sulfate to the oxalate concentration is about 128 to 1. This ratio falls off rapidly in an acid solution, having a value of 1.1 to 1 at a pH value of 2.5.

4. Miller's conclusion that the taking up of anions by hydrous oxide gels is a solid solution phenomenon has been disproven.

5. An investigation has been made of the taking up of the acid dyes, alizarin SW, alizarin, and orange II, and the basic dye, methylene blue, by hydrous oxide mordants at varying hydrogen-ion concentrations.

6. In every case lake formation consists in the adsorption of the colored ion by the hydrous oxides. There is no indication of the formation of definite chemical compounds between the dye and the mordant at any hydrogen-ion concentration.

7. The effect of varying the hydrogen-ion concentration on adsorption of the dye anion of the acid dyes is comparable throughout to the adsorption of sulfate or oxalate, provided the dye remains soluble.

8. The conclusion of Marker and Gordon that, at low pH values, ferric oxide and alumina react with orange II to form salts has been disproven. The presence of a high concentration of H_2SO_4 in the bath prevents the adsorption of the dye and causes it to be precipitated as the corresponding free acid. The alleged compounds proved to be mixtures of the hydrous oxides and the free orange II acid.

9. Methylene blue is adsorbed by the hydrous oxides only in case the dye bath is sufficiently basic to cause negative peptization of the mordant. The quantity of methylene blue adsorbed from the basic bath is shown to be a measure of the charge on the particles due to the adsorption of hydroxyl ions.

10. The formation of alizarin lakes from sodium alizarate baths is due to adsorption of the dye anion by the hydrous oxide and not to the adsorption of the neutral sodium alizarate as suggested by Bull and Adams and by Williamson, or to double decomposition between the dye and the oxide as proposed by Biltz in the case of ferric oxide.

11. The effect of sulfate ion on the adsorption of alizarin SW is similar to its effect on the adsorption of oxalate, sulfate replacing the dye if the bath is acid. The power of the sulfate ion to replace the dye cation decreases to zero as the bath becomes alkaline.

12. The effect of calcium ion on the formation of alizarin lakes is to increase the charge on the mordant, thereby enabling it to adsorb more of the dye anion rather than to remove sulfate from the bath, as suggested by Bancroft, or to form a complex calcium aluminum alizarate.

13. The salt effects in the mordanting process may be summarized as follows:

(a) The presence of a strongly adsorbed cation in the dye bath increases the rate and quantity of adsorption of acid dyes and has an oppo-

site effect on basic dyes, its effect increasing with the pH of the bath and with its own concentration.

(b) The presence of a strongly adsorbed anion in the dye bath decreases the rate and quantity of adsorption of acid dyes and increases the adsorption of basic dyes, its effectiveness increasing with the acidity of the solution and with its own concentration.

(c) If the dye bath is either acid or basic, the effects of the cations and anions are practically independent of each other, the influence of the cation predominating in the basic baths and the anion in the acid baths.

The above conclusions apply also to the dyeing of fiber in the absence of a mordant.

Department of Chemistry,
The Rice Institute,
Houston, Texas.

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